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PAPER

Enhancing moisture tolerance in efficient hybrid
3D/2D perovskite photovoltaics†

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Surface imperfections in perovskite films upon crystallization may trigger trap-assisted non-radiative recombination which is a dominant recombination mechanism that potentially restricts the performance of solar devices. In this work, 2D alkylammonium halide perovskites are formed on the 3D perovskite structure to passivate interfacial defects and vacancies and enhance moisture tolerance. The hybrid 3D/2D perovskite films possess longer photoluminescence lifetimes, as well as lower trap state densities, indicating the passivation of cationic and halide vacancies on the surface or grain boundaries, thereby reducing the non-radiative recombination pathways. More importantly, the hybrid 3D/2D perovskite exhibits higher ambient stability than a pure 3D perovskite where the hydrophobic nature of the long aliphatic carbon chains in the 2D perovskite provide an additional moisture repelling effect to the entire perovskite film. With this approach, the power conversion efficiency of perovskite solar cells was improved from 14.17% to 15.74% along with improved device stability. The hybrid 3D/2D perovskite solar cell retained 86% of its initial power conversion efficiency whereas the control device lost almost 40% of its overall efficiency. Thus, the hybrid 3D/2D perovskite structure is an alternative solution for modulating defects and trap-state densities in high efficiency perovskite solar cells with simultaneously enhanced moisture stability.

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Introduction

Organic–inorganic hybrid perovskite-based solar cells have revolutionized photovoltaics, and are able to achieve more than 22% power conversion efficiency^{1–6} and present an alternative to conventional silicon-based and other solution-processed

photovoltaics. The solution processability of perovskites provide their primary advantage over conventional silicon solar cells which are processed through high thermal budget protocols. However, the potential disadvantages of the solution-processed polycrystalline perovskites include structural disorder and crystallographic imperfections.^{7–9} Consequently, these surface and structural imperfections could lead to increased trap states and cationic/halide vacancies, which trigger trap-assisted non-radiative recombination and ion migration, detrimental to device performance.^{10–13}

The electrical quality of the perovskite surface layer (defects and vacancies) has been deduced to be the root cause for many of the challenges plaguing perovskite solar cells. These surface defects originate from uncoordinated Pb atoms created due to the liberation of volatile species such as methylammonium or iodide during thin film formation procedures. High surface trap state density has been attributed to current hysteresis effects, ion migration, impeded charge transport, lower charge extraction efficiency and significant interfacial recombination, limiting the performances of perovskite solar cells.^{14–18} Such imperfections are exclusively localized at the surface of the perovskite thin film; hence, passivation of these defects or vacancies plays a critical role in approaching bulk carrier dynamics of perovskites. The presence of defects also changes the surface chemistry of perovskite films, allowing for more

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rapid device degradation when exposed to water molecules.^{19,20} Exposed Pb atoms are the sites for PbX_2 -water complex formation which further releases halide anions which induced further perovskite film degradation.²¹

Constituting the perovskite from non-volatile, longer chain organic cations (as a replacement for MA^+ or FA^+) and thus forming 2D perovskites is considered as a promising material design strategy in reducing defects and, at the same time, promoting the stability.^{22,23} A previous study on the incorporation of an alkyl chain as a surface modifier shows great enhancement in hydrophobicity and barrier properties²⁴ whereby a similar strategy could also be implemented in a 2D perovskite containing alkylammonium organic cations. The presence of these hydrophobic organic cations offers “moisture shielding” effects to the perovskites and enhances their ambient stability. However, the power conversion efficiency of these lower dimensional perovskites is still limited due to large band gaps, higher exciton binding energy and poor charge transport due to their unfavourable tendency to crystallise with the organic layers perpendicular to the direction of charge transport.²⁵ Although nanostructuring or hot-casting of lower dimensional perovskite could possibly relieve the vertical charge transport issue, the overall conversion efficiency was still not comparable to those with 3D perovskites.^{26,27} Thus the ideal perovskite film architecture should consist of a 3D/2D bilayer architecture where the majority of the optical absorption and charge transport would occur in the 3D perovskite, whereas the thin 2D capping perovskite layer would act to reduce the surface defects and simultaneously avoid moisture ingress to achieve high efficiency stable perovskite photovoltaics.

In this work, we have designed such a 3D/2D hybrid perovskite structure by converting the top layer of a 3D perovskite into a thin 2D perovskite layer for high efficiency and stable perovskite photovoltaics. The 2D perovskite surface possesses low surface defects and vacancies and enhances the moisture tolerance. This hybrid perovskite exhibits water repelling properties and, more importantly, the trap states are significantly reduced while the photoluminescence lifetime is greatly enhanced, resulting in higher power conversion efficiency. The power conversion efficiency of the perovskite solar cell is enhanced from 14.17% to 15.74% utilizing an ambient stable hybrid 3D/2D perovskite absorber. Additionally, high efficiency devices are found to be accompanied with better device stability whereby the hybrid 3D/2D perovskite solar cell retained 86% of its initial power conversion efficiency while the typical 3D perovskite device lost almost 40% of its initial efficiency at 50% relative humidity.

Results and discussion

Surface defects and cationic/halide vacancies would tend to be created at the perovskite surface during the crystallization and/or annealing processes. To minimize the interfacial defects and vacancies, we formed 2D perovskites employing alkylammonium based iodide salts to modify the 3D perovskite ($\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$) surface. In terms of molecular interaction and charge balance, the positively charged

ammonium functional groups are able to passivate the cationic vacancies through hydrogen bonding between halide atoms and ammonium functional groups while the negatively charged iodide anions could passivate the halide vacancies, suppressing the recombination centers and resulting in a higher quality perovskite layer. Both butylammonium iodide (BAI) and octylammonium iodide (OAI) used in this study have been proven to form 2D layered perovskites by reacting with lead halides (PbX_2).^{28–30}

We investigated the formation of two different 2D perovskites with different alkyl chain lengths (butyl ammonium and octyl ammonium – Fig. S1†), and the effects of hybrid 3D/2D heterostructure on photovoltaic performances and moisture tolerance. The fabrication of a hybrid 3D/2D perovskite is illustrated in Fig. 1a, where BAI or OAI in isopropanol (IPA) is spun coat on top of the as-prepared 3D perovskite film [$\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$] and subsequently annealed at 100 °C for 15 min Fig. 1b shows the attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy of OAI-based hybrid 3D/2D perovskite films fabricated using different OAI concentrations. The CH_2 stretching bands are clearly identified in the range of 2850 to 3000 cm^{-1} , revealing the presence of the octylammonium cations in the perovskite film. Although some amine derivatives have also been utilized to passivate the surface of the perovskite,³¹ from the structural point of view, the positively charged ammonium functional group would interact more strongly with the surface terminal PbI_6^{4-} octahedra *via* hydrogen bonding while the iodide anions could passivate the iodide vacancies of the perovskite film. The optical absorption spectra of the BAI- and OAI-based perovskite films reveal the formation of 2D perovskites ($n = 1$) at 550–560 nm, leading to the hybrid 3D/2D perovskite structure. We deduce that BAI and OAI organic cations diffuse into the 3D

Fig. 1 (a) Fabrication of hybrid 3D/2D perovskites. (b) ATR-FTIR of the control perovskite and representative hybrid 3D/2D perovskites with different ammonium iodide concentrations. (c) Optical absorption and photoluminescence (PL) of a 3D perovskite and hybrid 3D/2D perovskites. The yellow shaded region indicates the formation of 2D perovskites with 10 mM BAI/OAI. (d) X-ray diffraction patterns of OAI-based hybrid 3D/2D perovskite films, indicating the increasing 2D perovskite formation with increasing OAI concentration.

perovskites, forming a thin 2D perovskite on the surface which acts as a moisture repelling layer for enhancing the stability of the entire film. Interestingly, the photoluminescence (PL) of 3D/2D hybrid perovskites was slightly red-shifted in 3D/2D perovskites probably due to partial surface functionalization by BAI or OAI and resulted in increased crystallinity in the perovskite film.^{32–34} As the concentration of OAI is increased, the emergence of X-ray diffraction peaks attributed to the layered perovskite is observed (Fig. 1d). We could estimate the d spacing to be 18.61 Å which agreed well with the reported value for $(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbI}_4$.^{29,35} This again indicates the reactivity of BAI and OAI in the bulk perovskite and the formation of 2D layered perovskites at the top surface.

In order to examine the water repelling behavior, we performed contact-angle tests on all the perovskite films. We find that the water contact angle for the standard 3D perovskite is 60.5° while the OAI-based 3D/2D perovskite films have significantly increased contact angles, beyond 90° (Fig. 2a). The OAI-based 3D/2D perovskite surface shows the best water repelling effect which could be attributed to its long hydrocarbon chain at the surface offering additional hydrophobicity. The greatly enhanced water contact angle also indicates high surface coverage of the alkylammonium cations over the perovskite film, changing its surface properties.

The increased water contact angle on the perovskite film provides a clue for the higher moisture tolerance in the hybrid 3D/2D perovskites. As depicted in Fig. 2b, the colour of the 3D perovskite film fades after prolonged exposure to a high humidity environment, with the 3D perovskite converting into PbI_2 . However, no significant change in the OAI-based 3D/2D

perovskite film is observed, indicating an improved moisture tolerance. The X-ray diffraction pattern of the 3D perovskite film reveals the formation of a large amount of PbI_2 as a product from the moisture-induced degradation process. The hydrophobicity from the OAI-based 3D/2D perovskite surface effectively prevents the perovskite from interacting with water molecules. It can be clearly concluded that the OAI-based 3D/2D perovskite film possesses higher moisture resistance which is essential for long term stability and practical application.

The inter-diffusion of the alkylammonium cations (butylammonium and octylammonium) into the 3D perovskite leads to structural and morphological changes. Top-view and cross-sectional SEM images of the standard 3D perovskite and the BAI/OAI-based hybrid 3D/2D perovskites are depicted in Fig. 3. The control perovskite displays a similar morphology with complete coverage and decent grain size as reported earlier.³⁶ Upon spin coating the alkylammonium iodide solution, the morphology and grain size are changed due to perovskite reconstruction during the formation of 2D perovskites upon annealing. It can be seen that the grain size of the perovskite is reduced. These cations easily diffuse into the perovskites and result in reconstruction of the perovskite structure which can be supported by the change in grain size observed from the cross-sectional SEM images in Fig. 3e and f.

In order to gain insight into the crystalline information, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements are conducted for the hybrid 3D/2D perovskite films. GIWAXS is perfectly suited to investigate crystal orientations in the perovskite films.³⁷ The 2D GIWAXS data for the control sample depict Debye–Scherrer rings as seen in Fig. 3g, which are associated with the tetragonal perovskite phase. In particular, the increased intensity of the (002)/(110) peak for q_{r}

Fig. 2 (a) Contact-angle test for the 3D perovskite and BAI- and OAI-based (10 mM) hybrid 3D/2D perovskites with water droplets. (b) Photographs of perovskite films, showing the enhanced moisture stability in the hybrid 3D/2D perovskites (10 mM BAI). The samples are stored at ~70% RH at ambient temperature. (c) X-ray diffraction patterns of 3D perovskite and hybrid 3D/2D perovskite films (shown in (b)), showing severe degradation in the 3D perovskite film. Asterisks denote the major reflections from PbI_2 .

Fig. 3 (a–c) Top-view and (d–f) cross-sectional view of field emission scanning electron microscope (FESEM) images of different perovskite films (10 mM BAI/OAI for 3D/2D perovskites) deposited on top of a mesoscopic TiO_2 layer. (g–i) GIWAXS data for the control and hybrid 3D/2D perovskites. 2D GIWAXS data for the control 3D perovskite with a highlighted (002)/(110) diffraction ring at $q = 1 \text{ \AA}^{-1}$. 2D GIWAXS data for the hybrid 3D/2D perovskites after the inclusion of 25 mM BAI and OAI, showing changes in the preferential crystal orientation of the system and additional highly ordered peaks for low q values, associated with the formation of 2D perovskites.

$\sim 0 \text{ \AA}^{-1}$ reveals a preferential crystal orientation parallel to the substrate. In addition, the characteristic (001) peak of PbI_2 at $q \sim 0.9 \text{ \AA}^{-1}$ is apparent due to the trace amount of PbI_2 added to the precursor solution for better perovskite film quality and device efficiency. The sample series with the inclusion of both BAI and OAI alters the crystalline nanostructure of the former 3D perovskite system. In the case of a low molar concentration of 10 mM BAI or OAI spun coat on top of the 3D perovskite structure, a reorientation of the crystal orientation is observed. Investigations by azimuthal integration around $q = 1 \text{ \AA}^{-1}$ reveal a decrease in face-up orientation, as seen in Fig. S2a.† Instead, dominating orientation peaks around $\chi = \sim 20^\circ$ and $\chi = \sim 55^\circ$ strongly contribute to the crystal orientation preference. Increasing the concentration of BAI and OAI further to 25 mM, reveals distinct features in the 2D GIWAXS data. First, the presence of highly ordered peaks at low q values indicates the formation of 2D perovskite with a strong crystal orientation parallel to the substrate, for both BAI at $q = \sim 0.31 \text{ \AA}^{-1}$ and OAI at $q = \sim 0.26 \text{ \AA}^{-1}$ (Fig. S2d and e†). Moreover, the presence of higher order peaks of the 2D perovskite indicates a well-defined system. As for the second feature, a further reorientation of the crystal nanostructure is observed, depicting an increase in face-up orientation of the (002)/(110) peak. Furthermore, due to the inclusion of BAI/OAI a decrease of the PbI_2 (001) peak is observed, indicating an enhanced conversion to perovskite in the probed samples for higher concentrations.

Generally, trap-assisted non-radiative recombination is the dominant recombination mechanism that potentially limits the performance of the solar devices.³⁸ The use of ammonium iodide salts to form the 2D perovskites could also passivate surface imperfections of the 3D perovskite layer and change the photoluminescence properties. The hybrid 3D/2D perovskite exhibits a longer photoluminescence (PL) lifetime (Fig. 4a), which could be an indication that the non-radiative recombination paths on the perovskite surface are suppressed. Since the PL lifetimes of perovskites can vary with morphology, we perform a supplementary measurement of the trap state density to quantify the passivation effects of the 2D perovskites. The trap-state densities of the perovskite films were examined by performing a power dependent steady-state photoluminescence measurement in the low fluence regime (where the Auger recombination is negligible). The trap state densities of each

perovskite film can be estimated by plotting the PL intensity as a function of photo-generated exciton density. The trap densities of the samples are estimated using a model used in our previous publications.³⁹ This model accounts for an infinite number of possible trapping pathways, each with their own trap densities. Since we are interested in investigating the trap density, we performed power-dependent photoluminescence measurements in the low fluence regime to prevent saturation of the traps and the results of the fit are summarised in Fig. 4b. The trap density (N_t) is highest in the control perovskite films, $2.3 \times 10^{17} \text{ cm}^{-3}$, which decreases in the hybrid 3D/2D perovskites. These findings thus validate our earlier hypothesis that the 2D perovskite layer in the hybrid 3D/2D perovskite reduces the trap-state densities.

To increase the device stability without sacrificing the overall conversion efficiency, 10 mM alkylammonium salts (BAI and OAI) are selected for fabricating the hybrid 3D/2D perovskite solar cells. We prepare perovskite solar cells with the unmodified 3D perovskite and two hybrid 3D/2D perovskites based on BAI and OAI. The solar cells are fabricated in the mesoscopic device configuration: FTO/compact- TiO_2 /meso- TiO_2 /perovskite/spiro-OMeTAD/Au. The J - V characteristics of the corresponding perovskite solar devices are illustrated in Fig. 5a while the summary of the photovoltaic parameters is given in Table 1. The control 3D perovskite solar cell has an average power conversion efficiency (PCE) of 14.17%, with a short-circuit current density (J_{sc}) of 19.99 mA cm^{-2} , an open-circuit voltage (V_{oc}) of 955 mV and a fill factor (FF) of 74.34%. With the hybrid 3D/2D approach, the PCE is increased to an average of 15.74% and 15.19% for the BAI- and OAI-based hybrid perovskites, respectively. The main enhancement in the photovoltaic parameters is the increase in the V_{oc} , which shows more than 10% enhancement, giving a V_{oc} of up to 1071 mV. Although long PL lifetimes need not necessarily equate to high performance cells, and OAI-based devices do not have exceptionally higher efficiencies

Fig. 4 (a) PL decay measurement of different perovskite films (10 mM BAI/OAI for 3D/2D perovskites). (b) PL intensity as a function of photo-generated exciton density within the low pump fluence range. The inset shows the power dependent steady-state photoluminescence in the low fluence regime (where there is negligible Auger recombination).

Fig. 5 (a) J - V characteristics of solar cells fabricated from various perovskite layers (10 mM BAI/OAI for 3D/2D perovskites), recorded in the reverse scanning direction (from V_{oc} to J_{sc}) with a sweep rate of 100 mV s^{-1} under AM 1.5G (100 mW cm^{-2}) illumination (mask = 0.09 cm^2). (b) IPCE and integrated current density of BAI-3D/2D perovskite solar cells. (c) Evaluation of photovoltaic parameters of unsealed mesoporous devices which were stored under $\sim 50\%$ relative humidity and dark conditions.

Table 1 Summary of PL lifetime (τ), trap densities (N_t) and device performances for 3D and hybrid 3D/2D perovskites (10 mM BAI/OAI)

	τ (ns)	$N_t (\times 10^{17} \text{ cm}^{-3})$	V_{oc} (mV)	J_{sc} (mA cm $^{-2}$)	FF (%)	η (%)
3D	46.2	2.3 ± 0.10	955 ± 19	19.99 ± 0.58	74.34 ± 2.81	14.17 ± 0.34
BAI-based hybrid	131	1.3 ± 0.10	1058 ± 13	19.40 ± 0.24	76.69 ± 0.57	15.74 ± 0.20
OAI-based hybrid	405	0.4 ± 0.05	1022 ± 16	19.37 ± 0.17	76.70 ± 0.72	15.19 ± 0.31

compared to BAI-based devices, our estimation of the trap-state density does indeed show a decrease in the OAI-based perovskite film compared to BAI-based and 3D perovskite films. This suggests that halide vacancies were passivated during the hybrid 3D/2D perovskite formation, which explains the increase in the PCE of the hybrid 3D/2D devices. Enhancement in V_{oc} was also observed in some purely iodide vacancy passivation studies.^{40–42} Interestingly, J_{sc} of the hybrid perovskite solar cells shows a value very close to those in control 3D perovskite devices, indicating that the newly formed 2D perovskite layer over the 3D perovskite would not restrict the interfacial charge injection. The long-term stability of the BAI-3D/2D hybrid perovskite was also confirmed by measuring stabilized photo-current density as a function of time measured at its maximum power point (0.83 V) under illumination for 1000 s, which is depicted in Fig. S7.†

The hybrid 3D/2D perovskite films were also examined for their moisture resistance in contrast to the typical 3D perovskite film. Fig. 5c illustrates the evaluation of the unsealed perovskite cells based on 3D and BAI-based hybrid 3D/2D perovskites. These unsealed devices are kept under high humidity conditions (RH > 50%) and tested periodically. Clearly, the hybrid 3D/2D perovskite device retains 86% of its initial efficiency while the conventional 3D perovskite device loses about 40% of its original conversion efficiency. For hybrid 3D/2D perovskite devices, the photovoltaic parameters such as J_{sc} , V_{oc} and FF retain 95%, 105% and 86% of their initial values. The key parameters causing the poorer performances in the 3D perovskite device are J_{sc} and FF. It can be deduced that the formation of a large amount of PbI_2 (evidenced from Fig. 2c) during the degradation process reduces the light harvesting, retards the charge transport and eventually increases the series resistance of the device. Thus, to ensure the long term stability of the perovskites with high power conversion efficiency, the hybrid 3D/2D approach emerges as an attractive solution.

Conclusions

In summary, the successful fabrication and characterization of hybrid 3D/2D perovskites and their photovoltaic application are demonstrated. The alkylammonium cations tend to diffuse into the existing perovskite film and reconstruct as a 2D perovskite at the surface of the 3D perovskite layer. The water repelling effect is greatly enhanced by this thin 2D perovskite over the 3D perovskite layer. The alkylammonium cations provide hydrophobicity which eventually delays the moisture-induced degradation of the perovskite and improves the moisture tolerance. At the same time, the iodide anions also passivate the halide vacancies whereby the non-radiative recombination pathway is

suppressed. By reducing the trap-state densities and filling up the vacancies, the PL lifetime is found to be much longer in the hybrid 3D/2D perovskite system. The PCE of the hybrid perovskite device is improved by 11% over the typical 3D perovskite device, reaching 15.94% of PCE. Importantly, the unsealed hybrid perovskite device retains 86% of its initial PCE while the standard 3D perovskite device loses 40% of its original PCE. Therefore, we have demonstrated a strategy to enhance the moisture tolerance and, at the same time, improve the PCE by implementing this hybrid 3D/2D perovskite approach, which is an attractive strategy in generating ambient stable perovskite solar cells without sacrificing its high efficiency.

Experimental

Butylammonium iodide (BAI) and octylammonium iodide (OAI) were synthesized by the following method. One equivalent of the corresponding amine (butylamine $\geq 99\%$ from Sigma Aldrich; octylamine 99% from Sigma Aldrich) was first dissolved in ethanol and cooled in an ice-bath for 15 min. 1.1 equivalents of hydriodic acid (57 wt% in H_2O) were subsequently added dropwise into the solution and kept stirring for 2 hours. The solution was then dried using a rotary evaporator at 60 °C. The resulting powder was recrystallized using ethanol and diethyl ether 5 times. The crystalline powder was obtained by suction filtration and washed thoroughly with diethyl ether. The powder was further dried under vacuum and stored in a glove box for use.

The perovskite solar cell devices were fabricated on fluorine-doped tin oxide (FTO) transparent conducting substrates with a mesoporous TiO_2 scaffold. The FTO substrates (Pilkington, TEC 15) were cut and cleaned by sequential 15-minute sonication in soap solution (Decon), deionized water and ethanol. Subsequently, the substrates were dried using a N_2 gun and treated with ozone plasma for 15 minutes. A compact TiO_2 blocking layer with a thickness of approximately 50 nm was deposited on the cleaned substrates by spray pyrolysis of a precursor solution on a 450 °C hot plate. The precursor is a solution of titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol, Sigma-Aldrich), acetylacetone and absolute ethanol with a volume ratio of 6 : 4 : 90. After cooling down to room temperature, the substrates were treated in a 50 mM TiCl_4 solution (5 M TiCl_4 from Wako Pure Chemical Industries, >99%, diluted with deionized water) at 70 °C for 30 min. A 250 nm-thick mesoporous TiO_2 scaffold was deposited by spin-coating a TiO_2 paste onto the dense TiO_2 -coated substrates. The TiO_2 paste was prepared by diluting a commercial TiO_2 paste (Dyesol 30NRD) and absolute ethanol in the weight ratio of 1 : 5 and stirring until the paste became homogenous. The diluted TiO_2

paste was spun coat at 4500 rpm for 30 s, followed by a three-step annealing procedure at 125 °C, 375 °C and 500 °C, each for 30 min.

The $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite layer was prepared according to a previous report.³⁶ Subsequently, the substrate was placed on a hot plate for annealing at 100 °C for 15 min. For the hybrid 3D/2D perovskites, 10 mM corresponding iodide salts (BAI and OAI) in isopropanol were spun coat on the perovskite layer at 4000 rpm for 30 s and the substrates were annealed at 100 °C for 15 min. After cooling down to room temperature, hole transporting materials, 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, Merck livlux SHT-263) solution, were deposited by spin-coating at 4000 rpm for 30 s. The spiro-OMeTAD solution was prepared by dissolving spiro-OMeTAD in chlorobenzene (100 mg ml⁻¹), with addition of 15.92 µl of *tert*-butylpyridine (96% from Sigma-Aldrich) and 9.68 µl of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI stock solution, 520 mg ml⁻¹ in acetonitrile) directly to the spiro-OMeTAD solution. Co-dopant tris(2-(1*H*-pyrazol-1-yl)-pyridine)cobalt(III) tris(trifluoromethylsulfonyl)imide (FK 102 Co(III) TFSI salt, Dyesol) was predissolved into acetonitrile and added to the hole-transport material solution at 15 mol% concentration. The as-prepared solution was spin-coated onto the perovskite film at 4000 rpm for 30 s. Finally, approximately 100 nm of gold electrode was deposited through a mask of 0.2 cm² using a thermal evaporator.

X-ray diffraction measurements were conducted on a Bruker AXS D8 ADVANCE system with Cu K α radiation ($\lambda = 1.5418$ Å). An incident angle of 5° was set to record the XRD spectra, with a step size of 0.05° and delay time of 1 s for each step. GIWAXS measurements were performed using a Ganesha 300XL SAXS-WAXS with an 8 keV Cu-K α X-ray source under vacuum. Data were collected at an incident angle of 0.4° and a sample-detector distance of around 106 mm with a Pilatus 300k detector. The data treatment of the GIWAXS measurements was conducted using the software GIXSGUI. Optical absorption was measured with a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu) in the wavelength range of 300–800 nm. SEM images of the perovskite films and devices were taken using a field emission scanning electron microscope (FESEM) JEOL JSM-7600F. For the moisture stability, perovskite films were deposited on mesoporous-TiO₂ substrates and kept under ~70% relative humidity at ambient temperature. The photovoltaic characteristics of the solar cell devices were measured in the reverse scanning direction (from V_{oc} to J_{sc}) with a sweep rate of 100 mV s⁻¹ under AM 1.5G (100 mW cm⁻²) spectrum by using a solar simulator (Newport 91190A) with a 450 W xenon lamp (model 81172, Oriel) calibrated with a Si reference cell (Oriel PN91150). The devices were characterized through a 0.09 cm² black mask. Incident photon-to-current efficiency (IPCE) was measured using a PVE300 (Bentham), with a dual xenon/quartz halogen light source, measured in DC mode and no bias light was used in the wavelength range of 300–800 nm. A Coherent OPerA Solo optical parametric amplifier pumped with a Coherent Libra™ regenerative amplifier (50 fs, 1 kHz, 800 nm) was used to generate a 600 nm excitation beam. Time-resolved

and steady-state photoluminescence of the samples was measured with a backscattering geometry at an angle of ~150° by using a collimating lens pair. The steady-state photoluminescence was measured using a fibre coupled to an Acton Spectra Pro 2500i spectrometer and a Princeton Instruments PIXIS 400B CCD camera. The time-resolved photoluminescence was measured by using an Acton Spectra Pro 2300i monochromator coupled to an Optronis Optoscope™ streak camera, which has a temporal resolution of ~10 ps. The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra of the perovskite films were measured using a PerkinElmer Frontier IR system. The contact angle between the perovskite films and the water droplets was measured using a Dataphysics OCA 15 Pro video-based optical contact angle measuring system.

Author contributions

N. M., S. G. M. and T. M. K. conceived the idea, designed the experiments and performed data analysis. V. S., X. G. and T. M. K. fabricated most of the devices and conducted the device and material characterization. S. S. L. and S. T. C. performed photophysical characterization. O. F., E. M. H. and P. M. B. conducted GIWAXS analysis. T. M. K. synthesized the relevant chemicals. T. M. K., N. M. and S. M. wrote the manuscript, and all authors discussed the results and commented on the manuscript. T. M. K. and V. S. contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

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