Surface roughness is a key parameter for judging the performance of a given material's surface quality for its electronic application. A powerful tool to measure surface roughness is 3D laser scanning confocal microscopy (LSM), which will allow you to assess roughness and compare production and finishing methods, and improve these methods based on mathematical models.

Focus on creating high-conductivity electronic devices with minimal power loss using laser scanning microscopy is an effective tool to discern a variety of roughness parameters.
Tuning the Surface Energy of Hole Transport Layers Based on Carbazole Self-Assembled Monolayers for Highly Efficient Sn/Pb Perovskite Solar Cells

Matteo Pitaro, Javier E. Sebastián Alonso, Lorenzo Di Mario, David García Romero, Karolina Tran, Jane Kardula, Teodor Zaharia, Malin B. Johansson, Erik M. J. Johansson, Ryan C. Chiechi, and Maria A. Loi*

Recently, carbazole-based self-assembled monolayers (SAMs) have been utilized as hole transport layers (HTLs) in perovskite solar cells. However, their application in Sn or mixed Sn/Pb perovskite cells has been hindered by the poor wettability of the perovskite precursor solution on the carbazole surface. Here a self-assembled bilayer (SAB) comprising a covalent monolayer (Br-2PACz) and a noncovalent wetting layer (4CzNH$_2$I) as the HTL in a Cs$_{0.25}$FA$_{0.75}$Sn$_{0.5}$Pb$_{0.5}$I$_{3}$ perovskite solar cell is proposed. It is demonstrated that the wetting layer completely solves the problem due to the higher polarity of the surface and, furthermore, the ammonium groups help in the passivation of trap states at the buried SAB/perovskite interface. The introduction of the SAB enhances the device reproducibility with an average efficiency of $18.98 \pm 0.28\%$ (19.45\% for the best device), compared to $11.54 \pm 9.36\%$ (19.34\% for the best device) for the SAM-only devices. Furthermore, the improved perovskite processability on the SAB helps to increase the reproducibility of larger device area, where a 12.5\% efficiency for a 0.8 cm$^2$ active area device compared to 0.68\% for the best SAM-based solar cell is demonstrated. Finally, the device’s operational stability is also improved to 358 hours ($T_{80\%}$), compared to 220 hours for the SAM-based solar cell.

1. Introduction

Organic–inorganic metal halide perovskite solar cells (PSCs) have seen exceptional improvements in device efficiency in the last years, reaching a record value of 26.08\%.[1] This rapid progress is generally attributed to the outstanding optoelectronic properties of the metal halide perovskites, such as the high absorption coefficient, low recombination rate, large carrier diffusion length, and good charge carrier mobility.[2–4] Despite these excellent qualities, PSCs are still far away from being commercialized. There are two main obstacles: the device stability, which is still far from the 25 years requested for rooftop installations, and difficulties in obtaining large-area devices of similar efficiencies as the small ones.[5,6] The challenge becomes even more complicated when also trying to reduce the environmental impact of the active layer by reducing the Pb content, for example by partially substituting it with Sn.[9] To date, the best performing mixed Sn/Pb perovskite solar cells (23.7%) implement a p-i-n structure, where poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) is used as a hole transport layer (HTL).[10,11] However, there are concerns about using PEDOT:PSS as HTL for these alloys, because of its hygroscopic and acidic nature that may affect the device’s long-term stability.[12] So far, only a few materials have been proposed as alternatives to PEDOT:PSS,[13–15]
Among them, poly[(bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) and nickel oxide (NiOx) have been successfully implemented as HTL in mixed Sn/Pb perovskite solar cells, with the only issue being poor device reproducibility. The reasons behind this poor reproducibility can be found in the hydrophobic nature of the PTAA surface, and in the chemical instability of NiOx when in contact with the perovskite layer.[16]

An alternative option to implement a more robust, efficient, and still commercially scalable HTL is by using carbazole-based self-assembled monolayers (SAMs). Carbazole-based monolayers have been widely used in Pb-based perovskite solar cells and silicon-perovskite tandem devices.[17–19] However, there are few reports on using SAMs as selective contacts in mixed Sn/Pb perovskite. To solve the perovskite solution wetting problem, we introduce a wetting layer composed by randomly oriented MPA-CPA molecules shows a homogeneous polycrystalline layer. To increase the hydrophilicity of the surface, which allows depositing a homogeneous perovskite layer. Interestingly, the ammonium iodide group can also have a passivation effect for the buried interface, reducing the surface defects that contribute to nonradiative recombination. Photoluminescence and time-resolved photoluminescence measurements show reduced nonradiative recombination at the SAB/perovskite interface. As a result of this improved interface, the open-circuit voltage of the fabricated solar cell increases from 0.81 to 0.82 V from SAMs to SABs. Furthermore, the reduced trap density, the reduced Sn\(^{4+}\) oxidation, and the reduced charge carrier recombination enhance the operational stability from 220 h for the SAM-based solar cell to 358 h \((T_{90\%})\) when the SAB is used. The most striking effect of using SABs as HTLs is related to the improved device scalability. When only the carbazole-based SAM is implemented in the device structure, we cannot deposit effectively the active layer on a 0.8 cm\(^2\) area. On the contrary, the SAB favors the full coverage of the device's active area with devices reaching efficiencies of 12.5%. It is important to note that the approach proposed here does not rely on any specific characteristic of the perovskite composition and therefore represents a general solution to the processability issue on carbazole-based SAMs, paving the way to the use of these SAMs in large-area devices.

2. Results and Discussion
We first implemented Br-2PACz molecules as HTL on ITO. To form a homogeneous monolayer, we selected a liquid phase deposition method instead of the commonly used spin coating technique.[21] As depicted in Figure 1a, the liquid phase deposition method consists of dipping a UV-O\(_3\)-treated ITO substrate in a Br-2PACz solution in ethanol for \(\approx 12\) h. This ensures a long enough chemical interaction between the ITO substrate and the Br-2PACz molecules to form a densely packed, ordered monolayer, as we described in our previous work.[23] The non-covalently attached molecules are removed by the washing step performed after the treatment. In this way, a homogeneous monolayer is obtained, as schematically represented in Figure 1a.[23] The final thickness of the Br-2PACz monolayer is \(\approx 1\) nm, as measured by variable angle spectroscopic ellipsometry, which is in agreement with the expected length of the molecule (\(\approx 1.1\) nm).

The nonpolar surface of carbazole-based SAMs causes a compatibility problem for the perovskite precursor solution, preventing the formation of a homogeneous perovskite layer. To increase the polarity of the HTL surface, and therefore the ability of the perovskite to form a homogeneous polycrystalline layer over the full substrate, we introduce a wetting layer composed of 4NH\(_3\)CzI molecules on top of the Br-2PACz, thus creating a self-assembled bilayer (SAB).[24] The driving force for the formation of the SAB is the \(\pi-\pi\) interactions of the two carbazole moieties. The ammonium iodide moiety of 4NH\(_3\)CzI decorates the surface at the ambient interface, increasing the hydrophilicity of the surface, which ensures the formation of a homogeneous monolayer, as we described in our previous work.[23] The authors claimed that by spin coating MPA-CPA they form a bilayer on ITO, consisting of a chemically anchored SAM plus a disordered overlayer. The overlayer composed by randomly oriented MPA-CPA molecules shows improved wetting characteristics for the Pb-based perovskite precursor solution.[26]

In this work, we implement a (2-(3,6-Dibromo-9H-carbazol-9-yl)ethyl)phosphonic acid (Br-2PACz) SAM as HTL in Cs\(\_2\)\(\_3\)FA\(\_3\)Sn\(\_3\)Pb\(\_3\)I\(_4\) perovskite solar cells. To solve the perovskite solution wetting problem, we introduce a wetting layer composed of a carbazole alkylammonium iodide derivative (4NH\(_3\)CzI) on top of Br-2PACz, creating a self-assembled bilayer (SAB).[25] The driving force for the formation of the SAB is the \(\pi-\pi\) interactions of the two carbazole moieties. The ammonium iodide moiety of 4NH\(_3\)CzI decorates the surface at the ambient interface, increasing the hydrophilicity of the surface, which allows depositing a homogeneous perovskite layer. Interestingly, the ammonium iodide group can also have a passivation effect for the buried interface, reducing the surface defects that contribute to nonradiative recombination. Photoluminescence and time-resolved photoluminescence measurements show reduced nonradiative recombination at the SAB/perovskite interface. As a result of this improved interface, the open-circuit voltage of the fabricated solar cell increases from 0.81 to 0.82 V from SAMs to SABs. Furthermore, the reduced trap density, the reduced Sn\(^{4+}\) oxidation, and the reduced charge carrier recombination enhance the operational stability from 220 h for the SAM-based solar cell to 358 h \((T_{90\%})\) when the SAB is used. The most striking effect of using SABs as HTLs is related to the improved device scalability. When only the carbazole-based SAM is implemented in the device structure, we cannot deposit effectively the active layer on a 0.8 cm\(^2\) area. On the contrary, the SAB favors the full coverage of the device's active area with devices reaching efficiencies of 12.5%. It is important to note that the approach proposed here does not rely on any specific characteristic of the perovskite composition and therefore represents a general solution to the processability issue on carbazole-based SAMs, paving the way to the use of these SAMs in large-area devices.
We deposited the wetting layer by spin coating a 1 mg/ml ethanol solution of 4CzNH$_3$I (Figure 1b). We hypothesize that the two carbazole bodies of Br-2PACz and 4CzNH$_3$I form a sandwich through $\pi$--$\pi$ interactions, giving rise to a surface of exposed ammonium groups, which drastically improves the wettability for the Cs$_{0.25}$FA$_{0.75}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ precursor solution in DMF and DMSO.

To properly investigate the perovskite precursor wettability on the Br-2PACz SAM and the SAB, we performed contact angle measurements using the Cs$_{0.25}$FA$_{0.75}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ solution (Figure 2a,b). As shown in Figure 2a, the contact angle of a perovskite solution droplet on the Br-2PACz monolayer is equal to 18.06°. On top of the SAB, the contact angle dramatically decreases to 3.29°, as shown in Figure 2b. This considerable switch towards a more polar surface confirms the formation of the SAB with exposed ammonium groups. It explains why a continuous perovskite film is obtained on this surface (inset of Figure 2b) while on the Br-2PACz monolayer the perovskite coverage is discontinuous (inset of Figure 2a). It is important to underline that it is also possible to modify the spin coating procedure for the perovskite films such that continuous films are obtained on Br-2PACz as well; however, this procedure is not easy to scale and is prone to mistakes that give reproducibility problems.\textsuperscript{23}

The photographs in the insets of Figure 2a,b were taken of films deposited by simple spin coating with antisolvent without the above-mentioned process modifications (see Experimental section).

To support the hypothesis of the formation of an ammonium-rich surface, we performed X-ray photoelectron spectroscopy (XPS) on ITO, ITO/Br-2PACz, and ITO/Br-2PACz/4CzNH$_3$I (Figure 2c–e and Figure S7a, Supporting Information). First, we analyzed the N1s core level spectra of SAM and SAB samples to understand the position of the ammonium groups coming from the 4CzNH$_3$I molecule (Figure 2c,d). The N1s spectrum for ITO/Br-2PACz shows a single and sharp peak located at 399.1 eV (Figure 2c).\textsuperscript{28} This peak arises from the C–N$\equiv$C bond of the Br-2PACz carbazole body, which reveals the presence of the molecules on the ITO surface. As expected, the N1s core level spectrum recorded on the SAB samples exhibits the same peak at 399.1 eV, with the addition of a second peak located at 400.8 eV (Figure 2d). This second signal emerges from the C-N$\equiv$C bond, revealing the presence of ammonium groups on the bilayer surface.\textsuperscript{28} This measurement therefore supports that the ammonium groups are exposed to the air interface because of $\pi$--$\pi$ interactions between the two carbazole bodies.

For a full characterization, we further compared the C1s spectra of the SAM and SAB samples with bare ITO substrate (Figure S7b, Supporting Information). It is important to notice that the 4CzNH$_3$I molecules contain carbon atoms with different chemical characteristics with respect to the SAM, which causes a new
Figure 2. Contact angle measurement schematics (top) and outcomes (bottom) for Cs$_{0.25}$FA$_{0.75}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite solution droplets on a) ITO/Br-2PACz and b) ITO/Br-2PACz/4CzNH$_3$I surface. In the insets are shown photographs of Cs$_{0.25}$FA$_{0.75}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite thin films deposited on ITO/Br-2PACz and ITO/Br-2PACz/4CzNH$_3$I substrates using spin coating. c,d) N1s XPS spectra recorded on (c) ITO/Br-2PACz (black line) and (d) ITO/Br-2PACz/4CzNH$_3$I samples (blue line). The green and red lines are the fitting for the C–N=C and C-NH$_3$ peaks, respectively. e) Br3d XPS spectra of ITO/Br-2PACz (black line), and ITO/Br-2PACz/4CzNH$_3$I samples (blue line).

Finally, we recorded the Br3d core spectra for the ITO/Br-2PACz and the ITO/Br-2PACz/4CzNH$_3$I sample, as shown in Figure 2e. The spectrum recorded on a SAM sample shows a single peak located at 69.2 eV (black line). When the SAB is formed, the peak is completely suppressed (blue line), indicating the formation of a homogeneous 4CzNH$_3$I layer. Finally, to prove the general application of this method, we performed XPS and contact angle measurements also on ITO coated with 2PACz monolayer and the proposed wetting layer (Figure S9a-d, Supporting Information). This analysis exactly overlaps with the...
one performed for Br-2PACz, revealing the general validity of this approach for carbazole-based monolayers.

To further prove the formation of π–π interactions between Br-2PACz and 4CzNH3I molecules, we simulated three different geometries using density function theory calculations at the B3LYP/TZP level with AMS-ADF (π-halogen, face-on, and off-set) and variable angle spectroscopic ellipsometry (SE) (Figure S10, Supporting Information). The more positive work function value is a further indication of the presence of positively charged ammonium groups located at the SAB surface.

Before fabricating complete solar cells with the implementation of the SAB, the physical properties of Cs0.25FA0.75Sn0.5Pb0.5I3 perovskite films deposited on both SAM and SAB were investigated.

In general, the perovskite grown on Br-2PACz/4CzNH3I samples exhibits similar optical and morphological properties compared to the one on Br-2PACz SAM samples. In fact, the absorption spectrum remains almost unchanged when the material is deposited on the Br-2PACz and on the SAB, with a negligible difference in optical bandgap (1.26 eV for the SAM and 1.25 eV for the full SAB, see Figure S14, Supporting Information). In addition, the formed SAB does not macroscopically affect the perovskite film crystallinity. In fact, X-ray diffraction measurements show that the perovskite films crystallize with a pseudocubic (Amml2) crystal structure when deposited on the Br-2PACz monolayer or the wetting layer, with a similar orientation towards (100) and (200) planes (Figure S15 and Table S1, Supporting Information). Finally, the AFM and SEM measurements reveal some differences in perovskite morphology on the two different layers (Figure S16 and S17, Supporting Information). The perovskite layers deposited on Br-2PACz SAB and on the SAB both exhibit a pinholes-free surface, with a roughness of ≈27 nm. Concerning the grain size, the perovskite deposited on the SAB shows an average grain size of 278 ± 91 nm, while on the SAB the average grain size is 794 ± 102 nm, potentially decreasing the trap density.[15] The increased grain dimension leads to a reduced overall dimension of the grain boundaries, which are the main locations of structural defects that act as recombination centers for charge carriers.[16] We believe that the larger grain size is a consequence of the enhanced polarity of the substrate (vide infra).

To further verify the quality of the active layer and the interaction with the new HTL, we performed steady-state and time-resolved photoluminescence (PL) spectroscopy exciting the perovskite films from their surface (top) and via the glass substrate (bottom) (Figure 3). First, by exciting the sample from the top surface (Figure 3a) we investigate the properties of the perovskite layer, a slightly higher PL peak intensity for the active layer deposited on the SAB compared to the one grown on SAM is revealed. This difference is not fully evident in the time-resolved PL measurements (notice that measurements are normalized at t = 0) which reveal similar charge carrier lifetimes between the perovskite deposited on Br-2PACz and the one on the SAB (Figure 3c). Excitations from this side of the sample mostly probe surface and bulk defects, indicating that the two samples are similar in that respect. However, excitations from the bottom of the sample, through the glass side (Figure 3b,d), probing the interface between the perovskite and the HTL, show a marked difference between the two samples. The PL peak of the perovskite film deposited on the SAB shows a higher intensity compared to the film fabricated on the Br-2PACz monolayer,

www.advancedsciencenews.com  www.afm-journal.de
Figure 3. Steady-state a,b) and time-resolved c,d) photoluminescence measurements performed on perovskite layers deposited on a Br-2PACz SAM (black curves) and on a Br-2PACz/4CzNH$_3$I SAB (blue curves) when probed through (a,c) the perovskite surface side or (b,d) the glass side.

and the time-resolved PL measurements are consistent with the steady state (Figure 3d). The charge-carrier lifetimes are 70.1 ns when the active layer is fabricated on SAM (Table S2, Supporting Information) and 76.4 ns when on the SAB. This improvement is mostly due to a longer initial decay ($\tau_1$). When exciting the sample from the HTL side we are not only probing the quality of the perovskite layer at the interface with the HTL but also the possible charge transfer to that layer. Here we could both argue that the buried interface is improved but also that the HTL is less effective. To decide which explanation is more plausible we should look at solar cells fabricated with the two different HTLs.

Devices were fabricated utilizing the p-i-n structure ITO/HTL/Cs$_{0.25}$FA$_{0.75}$Pb$_{0.5}$Sn$_{0.5}$I$_3$/C$_{60}$/BCP/Ag as shown in Figure 4a. The recording device fabricated using Br-2PACz monolayer as HTL exhibited a short-circuit current ($J_{SC}$) of 31.95 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.807 V, a fill-factor (FF) of 75.00%, and a power conversion efficiency (PCE) of 19.34% (Table S3, Supporting Information). The SAB-based record device exhibits a $J_{SC}$ of 31.61 mA cm$^{-2}$, a $V_{OC}$ of 0.819 V, a FF of 75.13%, and a PCE of 19.45% (Table S3, Supporting Information). The steady-state power output for the champion SAB-based device (Figure S18, Supporting Information) shows an efficiency of 19.2%, which is in agreement with the PL results and the hypothesis that the SAB is helping in the passivation of the buried interface. The limited difference in current density for the two device types is confirmed by the integrated current in the EQE measurements (31.54 and 31.14 mA cm$^{-2}$ for the SAM and SAB-based devices, respectively, see Figure 4c) and is statistically consistent. It is also interesting to note that the SAB-based devices show a lower leakage current, compared to SAM-only solar cells (inset of Figure 4b). This lower leakage current could be due to a reduced p-doping level of the Pb/Sn system. To verify this hypothesis, we performed impedance spectroscopy and Mott-Schottky analysis (Figure S19, Supporting Information). The Nyquist plots of our structures shown in Figure S19a, Supporting Information highlight that recombination mainly occurs in the perovskite bulk, as described by the single arch fitted using an RC element. The higher recombination resistance calculated for the SAB-based solar cells shows a reduced recombination in the perovskite bulk, which is consistent with the other analysis we have performed (Table S4, Supporting Information). The p-doping level is evaluated with a Mott-Schottky analysis (Figure S19b), which yields a lower background charge carrier density ($5.64 \times 10^{15}$ cm$^{-2}$) for the SAB-based devices.

However, besides small improvements in the details of the $J$–$V$ characteristics, the biggest improvement related to the use
Figure 4. a) Schematic representation (left) and cross-section SEM micrograph (right) of the device structure ITO/Br-2PACz/4CzNH₃I/perovskite/C₆₀/BCP/ITO. b) J-V characteristics and c) EQE spectra for SAM-based (black curve) and SAB-based (blue curve) solar cells. The dark J-V characteristics are shown in the inset. d) Box charts for the PCE values of Br-2PACz- (black symbols) and Br-2PACz/4CzNH₃I-based devices (blue symbols). A total of 20 devices were fabricated.

of the SAB as HTL is the widely improved device statistics, as reported in Figure 4d and Figure S20a–c, Supporting Information. The SAM-based devices present an average PCE of 11.54 ± 9.36% with a bimodal distribution composed of devices displaying about 19% efficiency and devices not working at all, while the SAB-based solar cells exhibit an average PCE of 18.99 ± 0.29%. Obviously, the large number of non-functional devices fabricated using Br-2PACz as HTL is caused by the poor wettability of this surface for the perovskite solution, giving rise to many device areas that are left uncovered during the spin coating deposition. In the case of SAB, the perovskite solution is readily spread, giving rise to full substrate coverage, and a very narrow performance distribution over more than 20 fabricated devices.

To conclude our analysis, we studied the device stability and scalability (Figure 5). The operational stability of encapsulated devices in air was evaluated by tracking the maximum power point under 100 mW cm⁻² illumination. The stability of solar cells fabricated using the SABs was largely improved compared to those on SAMs, with the champion SAB-based solar cell retaining 80% of its initial efficiency (T₈₀%) after 358 h compared to 220 h for the best reference SAM-based device. The main reason for this higher stability is revealed by XPS measurements performed
on the perovskite surface grown on the two different HTLs (Figure S21a, Supporting Information). The reduced full-width half maximum and the shift towards higher energy of the two Sn 3d_{3/2} and Sn 3d_{5/2} core levels peaks for the perovskite deposited on the SAB reveals a lower amount of Sn^{4+} on the surface. The deconvolution of the Sn 3d_{5/2} peak for the Sn^{2+} and Sn^{4+} signals shows that the Sn^{4+} content on the perovskite surface deposited on the SAB is reduced to 9.6% compared to 15.6% for the active layer deposited on the SAM (Figure S21b; Table S5-S6, Supporting Information).

Finally, solving the perovskite solution wettability problem is essential for scaling up the surface area of SAM-based solar cells. We, therefore, investigated the device scalability by fabricating solar cells with an active area of 0.25 cm² and 0.8 cm² (Figure 5b,c), which is up to factor 20 larger than the devices reported in Figure 4, which have an area of 0.04 cm². Again, we find that when Br-2PACz is used as HTL, a full coverage of the active area with the perovskite film is challenging (Figure 5b inset). Efficiencies of 0.02% and 0.68% for 0.25 cm² and 0.8 cm² active areas were recorded, respectively. When 4CzNH₃I molecules were implemented to form the SAB, efficiencies of 15.76% and 12.5% for the 0.25 cm² and 0.8 cm² active areas were measured, respectively. These results show the promise of the self-assembly bilayer for the fabrication of large-area Sn/Pb perovskite solar cells with carbazole-based HTLs.

3. Conclusions

We presented a route to improving the deposition of Sn/Pb perovskite active layers onto carbazole-based HTLs. By depositing 4NH₃ICz onto a Br-2PACz SAM, we can tune the surface energy from nonpolar to a more polar one. This allows depositing from solution Sn/Pb perovskite thin films of high quality with high reproducibility and reliability. Solar cells fabricated utilizing the bilayer as HTL show a higher V_{OC} of 0.82 V compared to 0.81 V for the SAM-based devices. This is ascribed to the higher bulk recombination resistance, lower dark current leakage, lower Sn^{4+} content, and passivation of defects at the buried interface. Furthermore, higher operational stability is observed, with SAB-based solar cells reaching T_{80%} after 358 h compared to 220 h for the SAM-based cells. Finally, the improved perovskite solution processability on the SAB helps to increase the reproducibility of larger area devices, where we demonstrate 12.5% efficiency compared to 15.76% for the best SAM-based solar cell for a 0.8 cm² active area device. This work provides a new toolbox to solve the large area scalability for devices utilizing carbazole-based SAMs as HTL, reopening considerations on their possible industrial use.

Supporting Information

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

Acknowledgements

The authors kindly acknowledge A. Kamp for technical support and for designing the device structure. The authors acknowledge Dynamo for providing materials for this study. This work is part of the Netherlands Organization for Scientific Research (NWO) – focus Group “Next Generation

Conflict of Interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Carbazole-based SAMs, mixed Sn/Pb perovskites, perovskite solar cells, scalability, stability, wettablity problem

Received: June 10, 2023
Revised: July 31, 2023
Published online: