**Enhancing the stability of perovskite solar cells through functionalisation of metal oxide transport layers with self-assembled monolayers**

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**Abstract**

A systematic study of the application of self-assembly monolayers (SAMs) onto electron and hole transporting layers for perovskite solar cells (PSCs) stability is reported. Cs0.05FA0.83MA0.17Pb(I0.87Br0.13)3 (FMC) perovskite films were deposited onto tin oxide (SnO2) and nickel oxide (NiOx) layers that were functionalized with ethylphosphonic acid (EPA) and 4-bromobenzoic acid (BBA) SAMs. X-ray diffractometry measurements were performed on these films shortly after they were deposited. The diffractograms agree with the positions reported in the literature for the crystal structure of the FMC. The results show that the deposition of SAMs on the metal oxide layers yields positive improvements in the FMC film stability and in the device stability when using FMC as the active layer. The work shows that by adopting SAMs, the long-term stability of PSCs cells under accelerated test conditions can be enhanced, and this provides one step on the way to making this technology a commercial reality.

**Keywords:** Self-Assembly Monolayer, Degradation Study, Perovskite Film, Perovskites Device, Light induced degradation, Temperature induced degradation.

**1. Introduction**

Perovskite Solar Cells (PSCs) are among the most promising emerging PV technologies, especially when used in high-efficiency multi-junction architectures and show a power conversion efficiency (PCE) which can match many mature technologies. The PCE of these potentially inexpensive, solution-processable devices has now reached over 25% in a single junction PSC and 28% in a perovskite-on-silicon tandem(Bauer et al., 2013). However, problems related to stability and upscaling still need to be overcome for commercialization of photovoltaic panels based on perovskites (Rong et al., 2018). These materials are very susceptible to moisture, UV light and heat, which cause degradation to the perovskite thin films and deterioration of the electrical properties of the devices(Ono et al., 2018). Several strategies have already been reported in order to extend the lifetime of photovoltaic devices based on hybrid perovskites: optimizing cation(Shukla et al., 2017) and halides(Noh et al., 2013) composition, altering the electron or hole transporting layer (ETL and HTL, respectively), the electrodes choice (Habisreutinger et al., 2016), amongst others. Electron and hole transport layers (ETL and HTL, respectively) formed by metal oxides (MOx) significantly affect the device lifetime (Shin et al., 2019). Recent attempts have been made to functionalized MOx layers which has been shown to extend the lifetime of these devices in some cases (Chen et al., 2018; Kim et al., 2018; Yang et al., 2018). Functional self-assembled monolayers (SAMs) with suitable molecular structure can provide better energy band alignment at the interfaces and help defect passivation at the oxide surface (Mingorance et al., 2018; Zuo et al., 2015), as well as improve subsequent crystallization of the perovskite active layer(Guan et al., 2019).

SAMs have a head group-spacer-terminal group structure where the head (or anchoring) group binds to the substrate, while terminal (or functional) group reconfigurates the substrate surface for the perovskite film deposition. Headgroups can be silanes, amines, phosphonates, carboxylates, among others (Guan et al., 2019; Qiao and Zuo, 2018). The compounds used as SAMs in the present work, ethylphosphonic acid (EPA) and 4-bromobenzoic acid (BBA) were chosen because they are representative compounds of this class of materials.

SAMs usually cause improvements in electrical parameters, which contribute to increased efficiency (Han et al., 2019; Hou et al., 2018; Wang et al., 2017; Yang et al., 2017; Zuo et al., 2015). However, there are few reports on the stability of these devices under real operating conditions (temperature and light soaking). In this work, a study was made on the stability tests of films and devices (with both inverted and non-inverted structures), with and without self-assembled layers, at an operating temperature of 75 °C and continuous light incidence.WhilstSAMs (EPA and BBA) has been reported before, this paper investigates their stability in much greater detail and considers how the stability changes are impacted by the applications of the SAMs in inverted or non-inverted configuration. SAMs have been deposited on tin oxide (SnO2) and nickel oxide (NiOx) and the influence on the electrical performance and on the lifetime of solar cell devices has been quantified. Significant changes were observed in the evolution of the absorbance of Cs0.05FA0.83MA0.17Pb(I0.87Br0.13)3 (FMC) perovskite thin films with the irradiation time due to the introduction of SAMs. SAMs also provided different changes in electrical parameters (JSC, VOC, and FF) of the devices in terms of their chemical nature and their combination with the MOx layer. Finally, SAMs are shown to significantly affect the lifetime of perovskite-based devices, extending up to five times the device's T50% (time for efficiency to reach half of its initial value) in some cases.

**2. Experimental**

2.a – Materials and device preparation

Cesium iodide (CsI), lead(II) bromide (PbBr2), nickel(II) nitrate hexahydrate, bathcuporine (BCP), 4-bromobenzoic acid (BBA) and ethylphosphonic acid (EPA) were purchased from Sigma Aldrich. Methylammonium iodide (MAI), formamidinium iodide (FAI), lead iodide (PbI2), and spiro-MeOTAD were purchased from Lumtec. Tin(IV) oxide, 15% in H20 were purchased from Alfa Aesar and PC61BM was bought from Nano-C. Both SAM solutions were dissolved in methanol with concentration of 0.5 mg.ml-1. The perovskite (FMC) solution was prepared by using 26 mg of CsI, 32 mg MAI, 92 mg PbBr2, 121 mg FAI and 346 mg PbI2 dissolved in 1 ml in DMF. The solution was stirred overnight at 70oC.

Glass/ITO (15Ω/square) substrates were cleaned with deionized water, acetone and isopropyl alcohol (IPA), and then treated with oxygen plasma for 5 minutes. For non-inverted devices, SnO2 layer was deposited by spin-coating at 4000 rpm, 1000 rpm.s-1 for 40 seconds, and annealed at 150oC for 30 minutes. For inverted devices, 182 mg of nickel acetate hexahydrate was dissolved in 60 μl of ethalinediamine and 1 ml of ethylene glycol, and left stirring for 3 hours at 70°C. The solution was then deposited by spin-coating at 2000 rpm, 1000 rpm.s-1 for 90 seconds, and annealed at 300°C for 1 hour. SAMs were deposited by dripping a volume of 90 μL onto substrates with a wait time of 60 seconds and then spin-coating at 3000 rpm, 1500 rpm.s-1 for 30 seconds. After the annealing at 120oC for 15 minutes, samples were washed with methanol.

Films/devices were transferred to glovebox for FMC deposition. The deposition was made by spin-coating at 4000 rpm, 2000 rpm.s-1 for 20 s and then at the final 5 s 90 μL of toluene was dispersed onto FMC solution, followed by annealing at 100oC for 1 hour. For non-inverted devices, spiro-MeOTAD was dissolved using 90 mg in chlorobenzene and doped with 30 μl of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI – 200 mg dissolved in 1 ml of acetonitrile), and 15μl 4-tert-butylpyridine. The solution were then filtered and deposited by spin-coating at 3000 rpm, 1500 rpm.s-1 for 30 s. For inverted devices, PC60BM was deposited onto the FMC later. Devices were then transferred for evaporation with 100 nm of Au or Ag deposited, depending of the structure of the device (according to Figure 1).

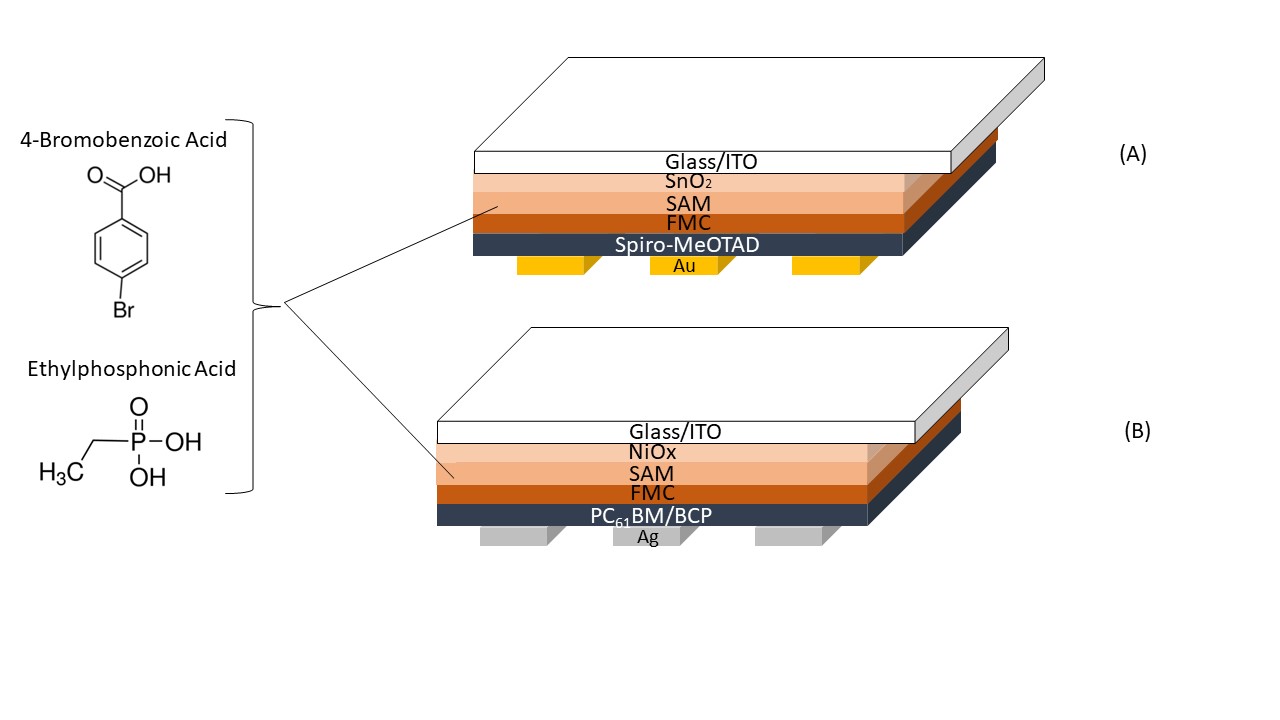


Figure 1 – Configurations for samples of films and devices. (A) Glass/SnO2/SAM/FMC film and Glass/ITO/SnO2/SAM/FMC/Spiro-MeOTAD/Au (non-inverted) device, (B) Glass/NiOx/SAM/FMC film and Glass/ITO/NiOx/SAM/FMC/PC61BM/BCP/Ag (inverted) device. A diagram of the energy levels for both device configurations is shown in figure S1 of the supplemental information (SI) file.

2b – Measurements

X-Ray Diffraction (XRD) measurements were made with a Panalytical Empyrean Powder diffractometer equipped with position-sensitive X’Celerator detector using Cu Kα radiation (λ = 1.5405 Å) and operated at 30 kV and 20 mA. UV-Vis absorption measurements were performed with the Ocean-Optics USB-4000 spectrometer using a Sulphur Lamp with intensity of 100 mW.cm-2 (calibrated using a silicon reference cell from RERA, Netherlands). The surface temperature of the substrate was monitored during the test at 75 oC. Devices were first tested using a Newport solar simulator with 100 mW/cm² AM 1.5G (calibrated using a silicon reference cell from RERA, Netherlands). Both films and devices were tested inside an air-tight chamber with optical windows and filled with nitrogen. The stability of the devices was then tested under sulphur-plasma irradiation.

**3. Results**

By considering the chemical structure of the head group-spacer-terminal group in the SAM compounds, it is expected that a strong chemical bond between the MOx surface and the phosphonic head group will be formed(Bauer et al., 2013). Nevertheless, it is the terminal group that can change the surface properties. Contact angle measurements were employed to evaluate the changes in the MOx surface due to SAMs deposition. The results of these measurements are shown in Table I. The most significant changes in contact angle occurred with BBA deposition, which creates approximately 2x and 5x increase in contact angle for SnO2 and NiOx treated films, respectively. Figure S2 (Supplemental File) shows the shape of water droplets formed on MOx surfaces before and after functionalization with SAMs.

Table I – Contact angle of water droplet on non-functionalized and functionalized metal oxides surfaces.

|  |  |  |  |
| --- | --- | --- | --- |
| Non-inverted device | Angle (°) | Inverted device | Angle (°) |
| SnO2 | 17 | NiOx | 14 |
| SnO2/Ethylphosphonic Acid (EPA) | 19 | NiOx/Ethylphosphonic Acid (EPA) | 27 |
| SnO2/4-Bromobenzoic Acid (BBA) | 30 | NiOx/4-Bromobenzoic Acid (BBA) | 68 |

The FMC perovskite films were then deposited on the MOx without and with SAMs. XRD measurements were performed on these films shortly after they were deposited. The diffractograms are shown in Figure 2. The 2θ position of the main peaks observed in these diffractograms agree with the positions reported in the literature for the crystal structure of the FMC (Shukla et al., 2017). From Fig. 2(a)-(c), it is evident that with the inclusion of SAMs on SnO2 films, there was an increase in FMC-related peak intensity, which is indicative of better FMC crystallization when deposited on functionalized MOx surfaces. However, the same was not true for FMC films deposited on NiOx (Fig. 2 (d) - (f)). In these cases, a peak is positioned at 12.6°, which is a characteristic of the residual PbI2 compound. This indicates that there is a segregation of this constituent in the FMC films deposited on NiOx, leading to the formation of PbI2 aggregates apart from the homogeneous FMC mixture. In addition, the FWHM of the FMC peaks deposited on NiOx is slightly higher than those deposited on SnO2, indicating that the perovskite crystals are smaller on NiOx (Islam et al., 2017).

Figure 2 – Diffractograms of FMC films deposited on non-functionalized and functionalized MO surfaces. (A) SnO2, (B) SnO2/Ethylphosphonic Acid, (C) SnO2/4-Bromobenzoic Acid, (D) NiOx, (E) NiOx/Ethylphosphonic Acid and (F) NiOx/4-Bromobenzoic Acid.



Initial studies were conducted in order to see how the absorption changed as a function of time during light soaking. Therefore, films were deposited and exposed to a 1 Sun of irradiance under a sulphur plasma lamp, in order to study the evolution of its optical absorbance as a function of photo-irradiation time. These measurements were performed in ambient atmosphere. The surface temperature was measured at 75 °C. Representative optical absorbances took during the light exposure at high temperature are shown in Figure S3. From these measurements, a parameter called Absorption Degradation State (ADS) was calculated, as discussed in (Misra et al., 2015). The ADS as a function of the irradiation time represents the degradation kinetics of the optical properties of the films.

Figure 3 shows the ADS changes ​​of the films as a function of the accumulated photo-irradiation dose. Based upon the data in figure 3, it is evident that FMC films deposited on NiOx are more stable, although the functionalisation with SAMs does not significantly alter this behaviour. The reason for this improved stability of FMC films deposited on NiOx may be related to the presence of PbI2 crystals found by XRD measurements. Melvin et. al recently reported that PbI2 can act as a filter for UV radiation in perovskite films (Melvin et al., 2018), so it is quite likely that the PbI2 is filtering this in films deposited on NiOx, thus reducing the degradation.

In contrast to the films deposited on NiOx, films deposited upon bare SnO2 exhibits a relatively rapid loss of its light absorbing properties. However, by functionalising the surface with a SAM, the stability is greatly enhanced; the EPA being the more effective of the two SAMs, in this case. These results indicate that the incorporation of SAMs in the MOx/perovskite interface may be beneficial for the longevity of devices with FMC as active layer.



Figure 3 – ADS of the FMC films as a function of accumulated dose of sulphur lamp irradiation.

Solar cells with non-inverted (with SnO2 as ETL) and inverted (with NiOx as HTL) configuration were manufactured to test the device performance and stability and the influence of the SAM functionalization. Figure 4 shows the characteristic JV curves of these devices. It is evident that there is stronger hysteresis for the device with a SnO2 ETL and that the functionalization with SAMs led to a significant decrease in this effect. Such hysteresis does not occur in inverted structure devices that employed NiOx as HTL, which agrees with previous reports (Wang et al., 2017). Thus, it is proven that the use of SAMs in planar devices having SnO2 as ETL is an effective mechanism to minimize hysteresis.

Figure 4 – JV curve for the best-perfoming devices (among five tested in each case) with planar non-inverted and inverted configuration. (A)ITO/SnO2/FMC/Spiro-MeOTAD/Au, (B) ITO/SnO2/Ethylphosphonic Acid/FMC/Spiro-MeOTAD/Au, (C) ITO/SnO2/4-Bromobenzoic Acid/FMC/Spiro-MeOTAD/Au, (D) ITO/NiOx/FMC/PC61BM/BCP/Ag, (E) ITO/NiOx/Ethylphosphonic Acid/FMC/ PC61BM/BCP/Ag, (F) ITO/NiOx/4-Bromobenzoic Acid/FMC/ PC61BM/BCP/Ag.



Table II shows the values ​​of the electrical parameters extracted from the J-V curves shown in Fig. 4. For non-inverted structures, the EPA leads to an improvement in the VOC, while BBA produced better fill factor and efficiency when compared to the device with EPA. By contrast, it can be observed a slight improvement in the current density values with EPA functionalization in the inverted structure device. Despite of these changes, it can be seen that, in both non-inverted and inverted structure, the surface functionalization of the MOx did not lead to substantially better values of PCE in the devices. Generally it is expected that the performance of the PSCs should increase after surface modification using SAMs. However, our results contradict this view, although our results are supported by other studies that show no improvement or a worsening in the electrical properties of the devices; examples include (Wang et al., 2017; Zuo et al., 2017)and(Hill et al., 2019).

Table II – Electrical parameters extracted of the JV curves of the best-performing devices, according to Figure 4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| SnO2 (non-inverted structure) | | | | | | |
|  | None | | Ethylphosphonic Acid | | 4-Bromobenzoic Acid | |
|  | Reverse | Forward | Reverse | Forward | Reverse | Forward |
| Voc (V) | 0.99 | 0.91 | 1.03 | 1.06 | 0.96 | 0.91 |
| Jsc (mA.cm-2) | 14.7 | 16.7 | 16.7 | 16.5 | 16.4 | 18.6 |
| FF (%) | 61 | 42 | 46 | 50 | 63 | 55 |
| PCE (%) | 10.3 | 6.4 | 7.9 | 8.7 | 9.9 | 9.3 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| NiOx (inverted structure) | | | | | | |
|  | None | | Ethylphosphonic Acid | | 4-Bromobenzoic Acid | |
|  | Reverse | Forward | Reverse | Forward | Reverse | Forward |
| Voc (V) | 1.06 | 1.05 | 1.03 | 1.01 | 1.01 | 0.99 |
| Jsc (mA.cm-2) | 18.5 | 18.5 | 19.5 | 19.8 | 17.6 | 17.7 |
| FF (%) | 67 | 70 | 65 | 64 | 66 | 72 |
| PCE (%) | 13.1 | 13.6 | 13.0 | 12.9 | 11.8 | 12.6 |

After J-V characterisation, the stability was studied in accordance with the ISOS-L-2(David et al., 2019; Khenkin et al., 2020) in an inert atmosphere chamber with sulphur plasma lamp irradiation. The temperature on the device surface was monitored as 75 °C during the tests. JV curves were collected periodically over the time of light exposure, in order to follow the evolution of the electrical parameters of the devices. The evolution of device efficiency as a function of photo-irradiation time is shown in Figure 5. It can be clearly observed that the use of SAMs lead to better stability, especially non-inverted devices using SnO2 as ETL and EPA as the SAM. Figure S4 shows the dependence of VOC, JSC and FF parameters on the irradiation time. It is evident that the decrease in efficiency was predominantly determined by the decrease of JSC with the photo-irradiation time.

Figure 5 – Comparison between the normalized efficiencies of the devices as a function of the irradiation time. (A) squares: ITO/SnO2/FMC/Spiro-MeOTAD/Au, circles: ITO/SnO2/Ethylphosphonic Acid/FMC/Spiro-MeOTAD/Au and triangles: ITO/SnO2/4-Bromobenzoic Acid/FMC/Spiro-MeOTAD/Au. (B) squares: ITO/NiOx/FMC/PC61BM/BCP/Ag, circles: ITO/NiOx/Ethylphosphonic Acid/FMC/ PC61BM/BCP/Ag and triangles: ITO/NiOx/4-Bromobenzoic Acid/FMC/ PC61BM/BCP/Ag.

Table III contains the T80% and T50% values ​​of the devices obtained from the data in figure 5. Based upon the data within the table, the effectiveness of employing the SAMs is quite apparent. However the T50% values ​​were limited to around 13 h in the best cases, which are relatively low compared to values ​​reported previously(Islam et al., 2017). However, in this analysis it is necessary to consider that the stability tests were performed under sulphur plasma and were not encapsulated. The sulphur plasma lamp is specified to Class A so possesses UV light. In addition, the sample temperature was around 75 °C. Under these conditions, the organic layers (Spiro-meOTAD in the case of the non-inverted structure, PCBM/BCP in the case of the inverted structure, see Fig. 1), in contact with the metallic electrodes, may suffer a rapid degradation of their electronic properties (Brinkmann et al., 2017; Mesquita et al., 2019; Weerasinghe et al., 2015), affecting irreversibly the electrical parameters of the devices.

Table III – T80% and T50% factors for the devices analysed in this work.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | SnO2 | | | NiOx | | |
| Time (hours) | None | Ethylphosphonic Acid | 4-Bromobenzoic Acid | None | Ethylphosphonic Acid | 4-Bromobenzoic Acid |
| T80% | 0.4 | 7.0 | 2 | 6.3 | 7.1 | 8.3 |
| T50% | 2.5 | 13.0 | 3.5 | 8.0 | 12.3 | 13.2 |

**4. Discussion**

Based upon data from the contact angle measurement, it is apparent that the surface functionalization of the SnO2 film with EPA had very little effect. However, the stability studies show that the inclusion of EPA at the SnO2/FMC interface has a significant positive effect upon the stability. For NiOx, the higher contact angle was observed after functionalization with BBA SAM, and the inverted device with this functionalised interface showed better stability in comparison with non-functionalized interface device. Such results show that the stability of the perovskite film and device seems not to be correlated with the hydrophilicity degree of the MOx surface. Wang et al. also have observed that devices with BBA SAM showed moderate improvement in stability of inverted structure devices when tested in the dark (Wang et al., 2017). In other work, the use of phosphonic acids as SAM in devices employing SnO2 as ETL provided a decrease in hysteresis and a significant increase in device longevity were reported (Weerasinghe et al., 2015), in agreement with the results obtained in the present work. Recent reports show that various effects may arise from the interaction between perovskite films and different functional groups of SAMs on which the films are deposited. These effects include improved film crystallization (Hou et al., 2018), defect passivation (Guan et al., 2019), increased charge transport properties across the interface (Zuo et al., 2017), and better alignment between energy levels of the MOx materials and the perovskite compound (Wu et al., 2019).

As it is shown that the inclusion of SAMs increases the stability of FMC films against photo-irradiation effects, there is a clear correlation between the stability and the molecular structure of the applied SAM. The FMC film deposited on SnO2 functionalized with EPA had its absorbance preserved for a longer irradiation time when compared to the film deposited on non-functionalized SnO2. At the same time, the device having EPA-functionalized SnO2 as ETL also has higher longevity when compared to the device that employed non-functionalized SnO2 as ETL. Likewise, both the film and the device that used NiOx functionalized with BBA were the most stable among those with NiOx as HTL. It can thus be said that a proper matching between the anchoring group and the MOx surface on the one hand, and between the functional group and the perovskite layer on the other hand, is a valuable interfacial engineering strategy that will produce significant improvements in the performance of photovoltaic devices.

However, it can be noted, from the T80% and T50% values ​​reported in Table III, that the beneficial effects on device durability provided by SAMs at the MOx/perovskite interface have been shown to be limited. This is probably related to the deterioration of the organic layers employed at the other interface, that is, those in contact with the metal electrode. The thermal stress that the devices were subjected to during the stability test, combined with the incidence of UV radiation, may have led to this relatively rapid deterioration. Irreversible damage to the properties of these layers, such as Spiro-meOTAD layer de-doping (for direct-structure devices) and the Ag diffusion into the PCBM/BCP layer (in the case of inverted-structure devices) have been reported for devices containing these organic layers when exposed to UV radiation and subjected to high temperatures(Farooq et al., 2018; Wang et al., 2019). Thus, it can be inferred that, for irradiation times less than 13 h, the durability of the devices evaluated in the present work was limited by the deterioration of the interface involving the MOx films. However, for times longer than 13 h, the limiting factor for device longevity was the degradation of organic layers used as HTL (Spiro-meOTAD) and ETL (PCBM/BCP) in direct and inverted structures, respectively. Such degradation was accelerated due to the conditions (high temperatures combined with the deleterious effects of UV radiation emitted by the sulphur lamp) at which the devices were subjected during the stability tests.

In view of the results obtained in this work, the following analysis can be deduced: the XRD data did not demonstrate the influence of SAMs on the crystallinity of perovskite films. In addition, the electrical characterization shows that the inclusion of the SAMs did not provide improvement in the electrical parameters, which indicates that the SAMs used in this work did not improve either the charge extraction capacity through the interface with the transporting layers, nor did it provide a better matching of energy levels between metal oxides and perovskite. By contrast, it is evident that the inclusion of SAMs significant increase in the stability of the devices, and this is directly related to the slower deterioration of the optical properties of perovskite films when deposited on the functionalized surfaces of metal oxides. Thus, it is very likely that the perovskite films deposited on the SAMs have fewer defects and the lower concentration of defects lead to A slower degradation of the perovskite absorber film. Additionally, one can observe the beneficial effect of functionalising SnO2 layers with respect to reducing hysteresis in the IV characteristics. This again corroborates the view that defects are reduced in the absorber layer (Lee et al., 2017; Miller et al., 2016; Yu et al., 2016).

**5. Conclusion**

Increasing stability and durability is a pressing need for the commercialisation of perovskite-based photovoltaic devices. We show that interface engineering with the use of SAMs is a promising method for stability enhancement. Our work shows that the functionalisation does not necessarily lead to enhanced efficiency, but the stability is greatly enhanced and hysteresis of the films are reduced. The surfaces of SnO2 and NiOx films, deposited by solution, was functionalized by ethylphosphonic Acid and 4-bromobenzoic Acid. Both Cs0.05FA0.83MA0.17Pb(I0.87Br0.13)3 films and devices were manufactured and used for stability testing by light soaking. It is clear that the interfaces play a significant role in the degradation of perovskite solar cells. By adopting SAMs, the long-term stability of private solar cells under real application conditions can be enhanced, and this provides one step on the way to making this technology a commercial reality.

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