

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: http://www.elsevier.com/locate/solmat



Efficient and stable perovskite solar cells via shortwave infrared polymer passivation



Jian Xiong^a, Naresh Eedugurala^b, Yifang Qi^a, Wei Liu^a, Anthony R. Benasco^b, Qiqi Zhang^a, Sarah E. Morgan^b, Michael D. Blanton^b, Jason D. Azoulay^b, Qilin Dai^{a,*}

^a Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, MS, 39217, USA

^b Center for Optoelectronic Materials and Devices, School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, MS, 39406, USA

ARTICLE INFO

Keywords: Polymer Passivation Charge extraction Perovskite solar cells

ABSTRACT

Defect passivation plays an important role in the performance of perovskite solar cells (PSCs). Here, a narrow bandgap conjugated polymer with hole mobility of 3.4×10^{-4} cm² V⁻¹ s⁻¹ is utilized as a passivation agent in the fabrication of air-prepared PSCs. Theoretical calculations complemented by Fourier transform infrared absorption spectroscopy (FTIR) demonstrate that N, S and O atoms in the polymer can behave as Lewis bases, which interact with Pb defects in the MAPbI₃ films to passivate grain boundaries (GBs) and interface defects. These interactions synergistically promote an enhancement of the crystallinity and smoothness of the films. Solar cells fabricated with the polymer passivation layer exhibit average efficiencies of 18.7%–19.6% compared to an average of 16.7% for reference devices. Unencapsulated devices retained approximately 80% of their initial efficiency following 600 h of exposure in air, compared with ~30% for reference devices. The moisture stability of the devices was also dramatically improved owing to the long hydrophobic alkyl chains within the polymer. This study demonstrates that narrow bandgap materials with tailored functionality can dramatically improve the PCE and stability of PSCs and shed light on the design of the passivants that further improve film quality and device performance.

1. Introduction

Perovskite solar cells (PSCs) with power conversion efficiencies now approaching 25% have attracted significant attention since they enable low-temperature fabrication using solution-based processes [1,2], excellent optoelectronic properties, and flexibility in device design [3–5]. This contrasts with other leading photovoltaic technologies such as silicon (Si, avg. PCE ~22.5%), cadmium telluride (CdTe, avg. PCE ~14.5%), and copper indium gallium selenide (CIGS, avg. PCE ~18.7%) [6]. Moreover, PSCs are anticipated to have a shorter energy payback time when compared to other photovoltaic technologies [7]. However, the poor stability of organic-inorganic halide perovskite materials remains as a major obstacle toward their implementation [8]. With PCEs rapidly approaching those of Si and other mainstream technologies, and commercialization on the horizon, strategies for improving stability and efficiency are urgently needed [7,9].

Grain boundaries (GBs) are critical to the performance and stability of polycrystalline solar cells [8,10–13]. Structural defects, such as

dangling bonds and vacancies are formed at GBs and found on the surface of films as a result of preparation via solution-based processes and crystallization at low temperatures (<100 °C) [10]. Dangling bonds provide pathways for ion migration and act as charge trapping centers, leading to recombination, hindering charge transport and extraction, and decreasing device performance [14]. Perovskite films are highly susceptible to attack from moisture within GBs, leading to decomposition and poor device stability [8,10]. The migration of ions through GBs leads to their accumulation near metal electrodes resulting in subsequent corrosion [8,13]. In view of the importance and consequences of GBs, many efforts have sought to passivate these features or reduce their numbers so as to enhance the efficiency and stability of PSCs [15–20].

Reports have demonstrated that self-passivation using excess PbI₂ and methylammonium iodide (MAI) can reduce recombination losses at GBs [17,18]. However, these self-passivation methods are very sensitive to preparation conditions, such as solvent composition and the specific process utilized, resulting in difficulties associated with reproducibility [11]. Other studies have demonstrated that excess PbI₂ is detrimental to

https://doi.org/10.1016/j.solmat.2020.110862

Received 1 September 2020; Received in revised form 10 October 2020; Accepted 30 October 2020 Available online 2 November 2020 0927-0248/© 2020 Elsevier B.V. All rights reserved.

^{*} Corresponding author. *E-mail address:* qilin.dai@jsums.edu (Q. Dai).

the overall device stability [21,22]. Therefore, many other passivation agents have been developed to passivate GBs and the surface of perovskite films in order to improve performance [23]. Among these, organic materials are particularly attractive owing to their rich structural modularity, simple and straightforward application methods, and versatile passivation effects [24]. Small organic molecular materials with short linear alkaneamine groups can be incorporated into the perovskite lattice to enhance device stability [16,25]. Organic Lewis acids and bases, such as buckminsterfullerene (C₆₀) [6,6,26]-phenyl-C₆₁-butyric acid methyl ester (PCBM) [15], aminovaleric acid (AVA) derivatives [27], 2-mercaptopyridine (2-MP) [28], and D-4-tert-butylphenylalanine (D4TBP) [11] have efficiently reduced trap states of perovskite films giving rise to significant enhancements in performance. Polymeric materials, such as polyvinyl pyrrolidone (PVP) [29], poly (methyl methacrylate) (PMMA) [30], and polystyrene (PS) [31] can also significantly reduce charge recombination losses by passivation. The advantages of polymeric materials as passivating agents are numerous. First, long-chain polymers can not only serve to passivate GBs, but also to improve morphology, crystallinity, or grain sizes of the perovskite films [32–35]. Second, hydrophobic segments in the polymers can protect perovskite films from degradation by moisture [36,37]. Third, immobilization of long chain polymers in perovskite films stabilizes inter-grain cross-linking [10]. Although polymers offer advantageous properties, there are few reports related to the use of those with multifunctional properties such as high charge carrier mobility, hydrophobic features, and tailored functionality for specific defect passivation roles, which coalesce to improve the performance of perovskite films.

Here, we demonstrate that a narrow bandgap polymer (poly (4-(5-(4-(3,5-bis(dodecyloxy)benzylidene)-4*H*-cyclopenta [2,1-*b*:3,4-*b*]dithiophen-2-yl)thiophen-2-yl)-6,7-dioctyl-9-(thiophen-2-yl)- [1,2,5]thiadiazolo [3,4-g]quinoxaline) ("**IR-P**", Fig. 1a) introduced into PSCs through

solution-processes can effectively passivate GBs and the surfaces of the perovskite films. Salient structural features include a large number of S, N, and O atoms, which provides Lewis basic sites beneficial for defect passivation in the perovskite films [24]. The long hydrophobic alkyl chains present in high density along the polymer backbone are beneficial for improving moisture stability. Moreover, the extended conjugation in this material promotes a narrow bandgap ($E_g \sim 1.1$ eV) with an absorption maximum (λ_{max}) of 1050 nm. Unlike insulating polymers, **IR-P** has a relatively high hole mobility (μ_h) of 3.4 \times 10⁻⁴ cm² V⁻¹ s⁻¹, which synergistically promotes enhanced charge transport and extraction within the devices. Chen et al. used n-typed conjugated polymer poly (bithiophene imide) (PBTI) to passivate the grain boundaries to obtained high efficient inverted PSCs [35]. Compared to their work, our p-type IR-P has high hole mobility, and thus benefits the hole extraction and transport in the GBs. Thus, PBTI is suitable for inverted PSCs while IR-P is suitable for planar PSCs. In addition, the fluoresence quench of perovskite films is also observed due to charge transfer between perovskite films and p-type IR-P. Furthermore, IR-P has high transparency at the visible light, and its introduction will not cause any light loss

The effects of **IR-P** on the perovskite film properties and the corresponding device performance were systemically investigated. These results show that **IR-P** can enhance crystallinity and reduce the surface roughness of the MAPbI₃ films. The polymers are present in the GBs and on the surface of the perovskite films, which is beneficial to charge transport and extraction as well as trap state passivation. The performance and stability of the PSCs are enhanced due to polymer incorporation. Average PCEs of 18.69% with a champion PCE of 19.56% is achieved in **IR-P**-based PSCs, which represents a statistically significant enhancement of 12% when compared to reference devices. Meanwhile, devices passivated with **IR-P** retain about 80% of their initial efficiency



Fig. 1. (a) The molecular structure of IR-P. (b) Device configuration of PSCs with IR-P. (c)-(e) The FTIR spectra of IR-P, MAPbI₃ and MAPbI₃:IR-P.

after 600 h of exposure in ambient conditions in the absence of any encapsulation, compared to \sim 30% for reference devices. The moisture stability of the PSCs is dramatically improved owing to the presence of hydrophobic alkyl chains in the polymer.

2. Experiment

2.1. Materials

Lead iodide (PbI₂, 99%) was purchased from TCI America. 2,2,7,7tetrakis-(N,N-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD, 99%), bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI, 99%), 4-*tert*-butylpyridine (tBP, 96%) and methylammonium (MAI, 99.5%) dimethylformamide (DMF, 99.8%, super dry), dimethyl sulfoxide (DMSO, 99.8%, anhydrous), and chlorobenzene (CB, 99.8%, anhydrous) were purchased from Sigma-Aldrich. **IR-P** was synthesized according to previously reported procedures [38,39].

2.2. Device fabrication

FTO substrates were cleaned sequentially with detergent, acetone, deionized water, and ethanol with ultra-sonication for 15 min each, and then were dried by hot air and treated by ultraviolet-ozone (UVO) for 15 min. For preparation of electron transport layers (ETL), the substrates were immersed in a TiCl₄ solution (0.19 M in deionized water) at 70 °C for 45 min and then washed with distilled water and ethanol, followed by annealing at 200 °C for 30 min in air. Then, the perovskite precursor (1.08 mmol PbI2:1 mmol MAI in 1 mL DMF:DMSO (9:1 v/v) mixed solvent) was spin coated on the TiO₂ film at 4000 rpm for 30s. For the $\mbox{IR-P}$ modified perovskite films, 0.3 mg ml $^{-1}$ $\mbox{IR-P}$ in CB as the antisolvent was dropped onto substrates during the last 20 s of the spincoating process. The perovskite films without IR-P were also prepared with antisolvent process as reference. The films were then heated to 100 °C for 30 min. The spiro-OMeTAD solution was prepared according to literature procedures [40] and deposited on the perovskite films. Finally, a gold electrode with a thickness about 60 nm was thermally evaporated on the top of the spiro-OMeTAD. The active area of the cells was 0.10 cm^2 as defined by a shadow mask.

2.3. Characterization

The micromorphology of films was characterized by atomic force microscopy (AFM) (Bruker Dimension Icon Scanning Probe Microscope) and scanning electron microscopy (SEM) (FEI, Helios Nanolab 600i, USA). The crystallinity of the perovskite films was examined using an Xray diffraction system (XRD) (Rigaku, MiniFlex 600). UV-vis absorption spectra were collected using an UV-vis spectrophotometer (Cary 60, Agilent, USA). The steady photoluminescence (PL) spectra and time resolved PL (TRPL) spectra were obtained with fluorescence spectrophotometer (FluoroMax, Horiba) with TCSPC accessories under 460 nm light excitation. FTIR spectra were recorded using an infrared spectrometer (Spectrum Two FT-IR, PerkinElmer, USA). The electrochemical workstation (604E, CHI) was employed to measure the electrochemical impedance spectroscopy (EIS) of the devices. For EIS measurements, the devices impedance spectra were measured by applying 5 mV AC voltage whose frequency was swept from 1 Hz to 1 M Hz in the dark. The capacitance-voltage (C-V) curves were obtained using an electrochemical workstation with a disturbance pulse bias voltage of 50 mV. The current-voltage characteristics were measured using a Keithley 2400 sourcemeter (Keithley Instruments Inc.) under AM 1.5G simulated sunlight (100 mW cm⁻²) (Newport). The light intensity was calibrated using a Si solar cell (91150V, Newport).

3. Results and discussion

Fig. 1b illustrates the device structure, which has a configuration of

FTO/TiO₂/CH₃NH₃PbI₃:**IR-P**/Spiro-OMeTAD/Au. The electrostatic potential surface (EPS) of **IR-P** was calculated using density functional theory (DFT) at the B3LYP level of theory to investigate passivation effects (Fig. S1). The electrostatic potential distribution of S, O, and N atoms shows a low distribution around these heteroatoms, consistent with their enhanced electronegativity. The accumulation of electrons could act as Lewis base anchors to passivate Pb-based defects in the perovskite films [41].

FTIR measurments were carried out to study the interactions between the IR-P and MAPbI₃ films with the results shown in Fig. 1 c-e. In the fingerprint region of the FTIR spectrum of IR-P, there are three main absorption peaks at 722 cm^{-1} , 793 cm^{-1} and 828 cm^{-1} (Fig. 1c), which can be assigned to $-(CH_2)_n$ - [42], C-C bonds between rings [43] and aromatic CH out-of-plane bends [44], respectively. These three peaks also appear in the FTIR spectrum of the perovskite film with IR-P, which confirms the successful incorporation of the polymer within the perovskite film. The absorption peak of the asymmetric C-O-C stretch is located at 1159 cm^{-1} [45] in IR-P, while this peak shifts to 1168 cm^{-1} in the MAPbI₃ film (Fig. 1d). In addition, an additional broad peak at 1840 cm^{-1} appears in the MAPbI₃:**IR-P** film (Fig. 1e), which is similar to the passivation of PBTI [35]. The vibrational frequency in FTIR is proportional to the square root of the force constant in the harmonic motion of a diatomic model [10], the redshift of C-O-C stretch vibration means that the bonding of C–O is reduced [10], which may be attributed to the interactions between positive charged groups (for example Pb^{2+}) of perovskite and negative charged O atoms of IR-P. Furthermore, the FTIR peaks at 906 cm⁻¹ (CH3NH³⁺ rock) [46], 1577 cm⁻¹ (asymmetric NH³⁺ bend) [47], and 1465 cm⁻¹ (symmetric NH³⁺ bend) [47] also show small blue shift to 904 cm⁻¹, 1576 cm⁻¹ and 1462 cm⁻¹, respectively (Fig. 1c and e). The blue shift of the perovskite film peaks and red shift of IR-P peaks confirm that there are strong coordination interactions between the functional groups of IR-P and Pb defects in the perovskite films. The FTIR results suggest that IR-P can passivate the defects of the GBs and interfaces of MAPbI₃ films.

To investigate the impact of IR-P on the morphology of the perovskite films, SEM and AFM measurements were carried out for the MAPbI₃ films with and without IR-P, as shown in Fig. 2. The reference perovskite film without IR-P shows high film coverage and uniform morphology with apparent GBs (Fig. 2a) typical of perovskite films prepared using the antisolvent method [11,19,48]. Cracks are evident throughout the film (Fig. 2a, inset). Interestingly, the perovskite film modified with IR-P exhibits a more uniform and compact structure compared to the reference film (Fig. 2b). As can be seen from the high resolution SEM image of the IR-P modified perovskite film (inset of Fig. 2b), no cracks are observed. AFM results also confirm the morphology improvement in the IR-P modified films (Fig. 2c-f). The root mean square roughness (RMS) of the perovskite films without and with IR-P are 19.10 nm-16.10 nm, respectively. In thin-film devices, the smoothness of each layer is very important for the interface contact. The smooth surface of the perovskite films leads to the reduced interface resistance of the perovskite/spiro-OMeTAD and reduced charge recombination loss at the interface of perovskite/spiro-OMeTAD. It is reported that the smoothness of the perovskite films is very necessary to obtain high-quality interfaces and high PCEs [49,50]. Besides, the smoother surface is also favorable for enhancing the interfacial contact at the ETL/perovskite interface. The high magnification AFM phase images of MAPbI3 film and MAPbI3:IR-P are shown in Fig. 2e and f, respectively. The high resolution AFM images show detailed information in terms of grains and GBs. Fig. 2e shows more granular structures, resulting in discontinuous domains within the reference film, which is consistent with SEM results. This is likely responsible for the lower performance resulting from less electronic coherence and dominant charge recombination behavior. Fig. 2f shows fewer outlines of the GBs when depositing IR-P on the active film. The IR-P enhances the film properties and also displays a more continuous network by coating the top surface of the film. Thus, the polymer may deposit at the GBs and



Fig. 2. (a) and (b) SEM images of MAPbI₃ and MAPbI₃:**IR-P** films, respectively. (c) and (d) AFM topography images of the MAPbI₃ film and MAPbI₃:**IR-P** film, respectively. (e) and (f) show AFM phase images of the MAPbI₃ film and MAPbI₃:**IR-P** film, respectively. The insets in Fig. 2a and b are the corresponding high magnification SEM images.

upper surface of the films to passivate the active layer defects. In view of the low concentration of the **IR-P** of 0.3 mg ml⁻¹, the polymer has negligible impact on the perovskite crystal grain sizes.

Fig. 3a shows the UV-vis absorption spectra of the MAPbI₃ film and MAPbI₃:IR-P film. The two overlapping absorbance curves indicating that the IR-P does not influence or interfere with the absorption properties of the perovskite film. In addition, the IR-P exhibits a dominant infrared absorption peak at ~1000 nm (Fig. S2), which is not shown in the MAPbI₃:IR-P film (Fig. 3a). This indicates that the final amount of IR-P inside perovskite film is too small to impact the absorption properties of the perovskite film. In order to investigate the effects of IR-P on the crystallinity of MAPbI3 films, XRD measurements were performed and the results are shown in Fig. 3b. Three XRD peaks at $2\theta = 14.10^{\circ}$, 28.44° and 31.88° are observed in the two perovskite films, which correspond to (110), (220) and (310) crystal plans of cubic phase MAPbI₃, respectively. XRD results confirm that the MAPbI₃ crystal phase is not influenced by the addition of IR-P [51]. The intensities of (110) and (220) XRD peaks of the MAPbI3:IR-P film are higher than that of the reference MAPbI₃ film, indicating that IR-P incorporation improves the crystallinity of the perovskite films, consistent with reports of other additives used in perovskite films [30,52]. That crystallinity enhancement maybe related with the intermediate adduct forming by the PbI2 reaction with Lewis acid as previous reported [30]. The improved crystallinity is expected to be beneficial to charge transport within the films and to the corresponding device performance. In order to investigate the charge transport behavior between IR-P and MAPbI₃, PL and

TRPL spectra were collected for the reference MAPbI₃ film and MAPbI₃: **IR-P** film. Fig. 3c shows the PL spectra of MAPbI₃ and MAPbI₃:**IR-P** films on glass substrates under 460 nm excitation from both sides of the films (the glass side and the film side) and the schematic diagram of PL test is shown in Fig. S3. A strong PL peak at 765 nm is observed for the MAPbI₃ film as the excitation light is introduced from the film and glass side. It is well-established that the penetration depth of light of these wavelengths is far less (i.e. on the order of dozens of nm) than the thickness of the perovskite film (several hundred nm) [15]. Thus, the PL spectra measured from both sides provide film quality information in terms of trap states and charge recombination information. The PL intensity of the reference MAPbI₃

film measured from the glass side is stronger than that from the film side. It is possible that more non-radiative recombination losses are caused by surface trap states on the upper surface of the MAPbI₃ film compared to the bottom surface. This may be related to air introduced during the fabrication process. Interestingly, strong PL quenching is observed after **IR-P** incorporation for airside data (MAPb₃ from air side and MAPbI₃:IR-P from air side), indicative of efficient hole transport from MAPbI₃ to **IR-P** since **IR-P** is a p-type material with $\mu_h = 3.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [38], which is higher than that of spiro-OMeTAD ($\mu_h = 8.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [53]. We believe that **IR-P** may benefit charge separation in the films and charge transport around GBs. Meanwhile, the PL obtained from the glass side also shows significant quenching, indicating that **IR-P** is present throughout the whole film. Therefore, the **IR-P** incorporation provides an additional hole transport



Fig. 3. (a) UV–vis absorption spectra and (b) XRD patterns of the MAPbI₃ (reference) and MAPbI₃:**IR-P** films. (c) The PL spectra for the films with and without **IR-P** using 460 nm as excitation source form the film side (solid circles) and from the glass side (hollow circles). (d) TRPL spectra of the MAPbI₃:**IR-P** films.



Fig. 4. (a) The PCE values of the PSCs as a function of IR-P concentrations. (b) Typical J-V curves of the device with IR-P 0.3 mg ml⁻¹ and reference cell. (c) Stabilized PCE and J_{sc} of the PSC with IR-P and reference device. (d) PCE statistics of the PSCs with and without IR-P obtained from 30 devices for each experimental condition.

channel in PSCs due to its relatively high hole mobility. From Fig. 3d, the lifetime of MAPbI₃:**IR-P** is only 15.97 ns, which is much shorter than that of MAPbI₃ (139.83 ns). Fig. S4 shows the energy-level diagram for each component of PSCs. By introduction of this IR-P, there is another possible pathway for the hole transport in PSCs as the "②"in Fig. S4. The highest occupied molecule orbital (HOMO) energy level of IR-P is -4.8 eV, and the holes may transport from perovskite (HOMO is -5.4 eV) to IR-P then to Spiro-OMeTAD and Au. The PL and TRPL of the films of glass/MAPbI₃/Spiro-OMeTAD and glass/MAPbI₃:IR-P/Spiro-OMeTAD are also measured and the results are shown in Fig. S5. The PL intensity of glass/MAPbI₃/Spiro-OMeTAD. The average PL lifetime values of the glass/MAPbI₃/Spiro-OMeTAD and glass/MAPbI₃:IR-P/Spiro-OMeTAD are 4.04 ns and 3.10 ns. Thus, Thus, two charge extraction mechanisms from perovskite films by IR-P and Spiro-OMeTAD exist in the devices.

PSCs with the structure of FTO/TiO₂/MAPbI₃:IR-P/Spiro-OMeTAD/ Au were prepared, and the reference devices without IR-P fabricated for comparison. IR-P concentration-dependent PCE is shown in Fig. 4a. PCE for each concentration is derived from 8 devices prepared using the same experimental conditions. The detailed performance parameters of the devices are summarized in Table S1. The average PCE values of PSCs prepared with **IR-P** concentrations of 0, 0.1, 0.3, 1, 2 and 4 mg ml⁻¹ are 17.10%, 18.73%, 18.96%, 18.81%, 17.51%, and 15.88%, respectively, yielding an optimal concentration of 0.3 mg ml⁻¹. The average performance parameters of the PSCs based on 30 devices prepared under the same experimental condition are summarized in Table 1. PSCs without **IR-P** exhibit an average PCE of 16.69%, J_{sc} of 21.62 mA cm⁻², opencircuit voltage (Voc) of 1.03 V and fill factor (FF) of 74.68%. PSCs with IR-P show an average PCE of 18.69%, which is an enhancement of 12% when compared to the reference device. The J-V curves, stabilized PCE as well as short-circuit current density (Jsc) of the PSC with 0.3 mg ml⁻¹ IR-P and reference PSC under AM 1.5G one-sun illumination are shown in Fig. 4b and c. The optimal device with IR-P shows a high PCE of 19.56% (Fig. 4b). All the photovoltaic parameters including FF, J_{sc} and Voc are improved compared to that of the reference device. Typically, FF increases from 74.68% to 78.20%, and V_{oc} increases from 1.03 V to 1.07 V. J_{sc} increases from 21.62 mA cm⁻² to 22.41 mA cm⁻². The Voc, FF and Jsc enhancement may be attributed to the efficient trap state passivation including GBs and interfaces. In addition, the improved charge transport and extraction, due to the excellent hole transport property of IR-P also contribute to the improved J_{sc} and FF. Fig. 4d shows the PCE statistics of the PSCs with and without IR-P obtained from 30 devices for each condition. The PCE distribution range of IR-P treated devices is narrower than that of the reference devices, indicating that the repeatability of the device fabrication progress has been improved. IPCE spectra of the devices with and without IR-P in the infrared region are shown in Fig. S6. The minor increase of IPCE in the infrared region is attributed to the limited amount of IR-P in the devices. In addition, the hysteresis of the PSCs with IR-P also been reduced comparing with reference devices. Fig. S7 shows the J-V curves under reverse and forward scan directions, and the photovoltaic parameters are summarized in Table S2. The reference device shows serious hysteresis, and reduced hysteresis is observed by IR-P introduction. Although our devices show a hysteresis effect, this does not affect our IR-P modification strategy to improve device performance. Therefore, the improved device performance may be attributed to improved charge transport and extraction and defect passivation at GBs and interfaces by **IR-P** incorporation.

Table 1

Average photovoltaic parameters of PSCs with and without **IR-P**. The parameters of the champion devices are shown in brackets.

Sample	J_{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
Reference	21.62 (22.48)	1.03 (1.06)	74.68 (78.42)	16.69 (18.64)
With IR-P	22.41 (22.75)	1.07 (1.08)	78.20 (79.27)	18.69 (19.56)

To further understand the charge extraction and recombination behaviors in the devices, electrochemical impedance spectroscopy (EIS) was used to investigate the electrical dynamics of the PSCs. Fig. 5a shows the Nyquist plots of the PSCs based on reference MAPbI3 and MAPbI3:IR-P films, and the equivalent circuit used to fit the curves is shown in the inset of Fig. 5a. The low-frequency part is corresponding to the recombination resistance (R_{rec}) and chemical capacitance (CPE1) of the devices, while the high-frequency semicircle is associated to the contact impedance, R2 and CPE2, between the perovskite and two selective contacts [54]. In Fig. 5a, only one semicircle is observed, and the fitting values are listed in Table S3. Usually, the large radius of the semicircle indicates a large recombination resistance (R_{rec}) [55]. As can be seen from the fitting values, R_{rec} of the PSCs with IR-P (4893 $\Omega)$ is much higher than that of the reference device (1494 Ω). CPE1 value of IR-P-based device $(1.05 \times 10^{-5} \text{ F})$ at low frequency is smaller than that of reference device (7.96 \times 10⁻⁵ F), which may be related to the reduction of ions and electron accumulation at electrode interfaces or defect passivation of MAPbI₃ films by IR-P introduction [56]. This shows that the IR-P incorporation can reduce the defects and recombination loss in the device, which is consistent with the enhancement of Voc. The R_2 values is also decreased from 420 Ω to 384 Ω , which is attributed to the improved contact of perovskite/Spiro-OMeTAD by IR-P [40]. In addition, C-V data under dark conditions were used to examine the semiconductor properties of the PSCs. The C-V curves show typical Mott-Schottky contact behavior [57]. The built-in potential (Vbi) values obtained from Mott-Schottky curves (Fig. 5b) for the PSCs with IR-P and reference cell are 0.90 V and 0.85 V, respectively. The increased V_{bi} may benefit the charge extraction and reduce the charge recombination loss in the devices. This result also indicates that the trap sates in the film are greatly reduced by IR-P incorporation.

In order to quantitatively study the passivation effects of **IR-P** on the MAPbI₃ films, the trap density of states (tDOS) is calculated according to the following equation based on EIS data (Fig. 5a) and the C–V curves (Fig. 5b) [26,58]:

$$C = -\frac{1}{\omega Z^*} \tag{1}$$

$$N_t(E_{\omega}) = -\frac{V_{bi}}{\omega q} \frac{dC}{d\omega} \frac{\omega}{K_B T}$$
(2)

$$E_{\omega} = K_B T \ln(\frac{\omega_0}{\omega}) \tag{3}$$

where C is capacitance of the device; Z'' is the imaginary part of the impendence; ω is the angular frequency; N_t is the trap density; V_{bi} is the built-in potential; q is the elementary charge; K_B is the Boltzmann constant; T is the absolute temperature; ω_0 is the attempt-to-escape frequency ($\approx 10^{11} \text{ s}^{-1}$) [58]; and E_{ω} is the energy demarcation. Fig. 5c shows the tDOS of the PSCs with and without IR-P. The tDOS of the modified PSC is lower than that of the reference device within the energy range from 0.32 to 0.52 eV. This result shows that both the shallow and deep trap states are passivated by IR-P [26]. Consistent with SEM and AFM measurements, IR-P may fill in the GBs and modify perovskite interfaces. In addition, IR-P contains many long hydrophobic alkyl chains. Thus, IR-P can protect MAPbI3 from degradation by moisture due to the hydrophobic properties of the long alkyl chains, an umbrella effect [59]. To investigate the impact of IR-P on the stability of the devices, PSCs with and without IR-P were exposed to ambient conditions (with approximately 20-40% relative humidity) and the PCE tested at different intervals. As shown in Fig. 5d, the average PCE of PSCs with IR-P maintain about 80% of their initial value after 600 h of aging, while the reference devices maintain about 30%. There is a rapid drop in the efficiency during the first 100 h of exposure for the reference devices, which may be related to interface degradation [60], which is greatly reduced upon IR-P incorporation. Therefore, both the interface stability and film stability are greatly enhanced by IR-P. We use a



Fig. 5. (a) Nyquist plots of PSCs with and without IR-P measured at a bias of 0.9 V. (b) Mott-Schottky curves for the reference and IR-P treated PSC. (c) The tDOS for the PSCs with and without IR-P. (d) The stability of the PSCs with and without IR-P. The stability is derived from 6 devices.

hotplate to generate water vapor in a glove box to achieve a high humidity environment (RH~ 95%). Fig. S8a shows the setup, and the humidity is monitored by a hygrometer. The devices are kept in this box, and the J-V curves are tested at special intervals. The results are shown in Fig. S8b. Both devices show quickly decay under this harsh condition. The PCE values of reference devices drop by 84% after 5 h exposure. The PCE values of PSCs with IR-P drop by 48%, which shows improved moisture stability compared to the reference devices. This improvement may be attributed to the hydrophobic properties of IR-P (Fig. S8c). These systematic studies demonstrate that IR-P has a significant impact on perovskite film properties and the corresponding device performance. The functions of this polymer in enhancing the efficiency and stability of PSCs can be summarized into four main aspects. (i) IR-P improves the morphology of the perovskite film. IR-P introduction reduces cracks and surface roughness by distributing in GBs and coating the upper surface of the perovskite film. (ii) IR-P has large number of S, N and O atoms, which interact with Pb ions and act as Lewis base anchors to passivate the positive Pb-based defects in the GB and surface defects of the grains. (iii) IR-P can efficiently extract charge from the perovskite grains and also provide additional efficient hole transport pathways owing to its relativity high hole mobility. (iv) The stability of the PSCs is improved by the IR-P due to the hydrophobic properties of the long alkyl chains in the IR-P.

4. Conclusion

In this work, a polymer (**IR-P**) is used as an efficient passivation agent to enhance the PCE and stability of PSCs. **IR-P** can be incorporated within GBs and on the surface of the films, which leads to effective trap passivation and enhances charge transport and extraction in the devices. The relatively high hole mobility of the polymer also improves charge transport within the devices as evidenced through PL and TRPL measurements. The highest PCE of 19.56% and average PCE of 18.69% are

achieved for the PSCs with **IR-P** incorporation, which is an enhancement of 12% when compared to reference devices. In addition, the interface stability and film stability are greatly enhanced by **IR-P** introduction due to the hydrophobic groups in the polymer. PSCs with **IR-P** can retain about 80% of their initial efficiency after 600 h exposure in air without any encapsulation compared to ~30% for the reference devices.

CRediT authorship contribution statement

Jian Xiong: conceived the experiments and writing the original draft, All authors contributed to manuscript development. Naresh Eedugurala: contributed to polymer synthesis, All authors contributed to manuscript development. Yifang Qi: characterized the performance of the films and materials. All authors contributed to manuscript development. Wei Liu: contributed to theoretical simulation, All authors contributed to manuscript development. Anthony R. Benasco: characterized the performance of the films and materials, All authors contributed to manuscript development. Qiqi Zhang: characterized the performance of the films and materials, All authors contributed to manuscript development. Sarah E. Morgan: contributed to writing review & editing, All authors contributed to manuscript development. Michael D. Blanton: contributed to writing - review & editing, All authors contributed to manuscript development. Jason D. Azoulay: contributed to writing - review & editing, All authors contributed to manuscript development. Qilin Dai: contributed to project supervision, writing - review & editing of the manuscript, All authors contributed to manuscript development.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This material is based on work supported by the National Science Foundation [Grant No. 1757220], and NSF NRT Interface Award provided traineeship support for AB [Grant No. 1449999]. The steady state PL and TRPL equipment used in this work is supported by National Science Foundation Research Initiation [Grant No. 1900047]. QZ is supported by NSF-PREM [Grant No. DMR-1826886].

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.solmat.2020.110862.

References

- NREL, Best Research-Cell Efficiencies, 2019. https://www.nrel.gov/pv/cell-efficiency.html.
- [2] J. Xiong, B. Yang, R. Wu, C. Cao, Y. Huang, C. Liu, Z. Hu, H. Huang, Y. Gao, J. Yang, Efficient and non-hysteresis CH₃NH₃PbI₃/PCBM planar heterojunction solar cells, Org. Electron. 24 (2015) 106–112.
- [3] M. Kaltenbrunner, G. Adam, E.D. Głowacki, M. Drack, R. Schwödiauer, L. Leonat, D.H. Apaydin, H. Groiss, M.C. Scharber, M.S. White, N.S. Sariciftci, S. Bauer, Flexible high power-per-weight perovskite solar cells with chromium oxide-metal contacts for improved stability in air, Nat. Mater. 14 (2015) 1032–1039.
- [4] Y. Li, L. Ji, R. Liu, C. Zhang, C.H. Mak, X. Zou, H.H. Shen, S.Y. Leuf, H.Y. Hsu, A review on morphology engineering for highly efficient and stable hybrid perovskite solar cells,, J. Mater. Chem. A 6 (2018) 12842–12875.
- [5] X. Hu, Z. Huang, X. Zhou, P. Li, Y. Wang, Z. Huang, M. Su, W. Ren, F. Li, M. Li, Y. Chen, Y. Song, Wearable large-scale perovskite solar-power source via nanocellular scaffold, Adv. Mater. 29 (2017) 1703236.
- [6] International Energy Agency-Photovoltaic Power Systems Technology Collaboration Programme, National Survey Report of PV Power Applications in China, 2018. https://iea-pvps.org/publications/.
- [7] J. Gong, S.B. Darling, F. You, Perovskite photovoltaics: life-cycle assessment of energy and environmental impacts, Energy Environ. Sci. 8 (2015) 1953–1968.
- [8] J. Jiang, Q. Wang, Z. Jin, X. Zhang, J. Lei, H. Bin, Z. Zhang, Y. Li, S.F. Liu, Polymer doping for high-efficiency perovskite solar cells with improved moisture stability, Adv. Energy Mater. 8 (2017) 1701757.
- [9] Y. Rong, Y. Hu, A. Mei, H. Tan, M.I. Saidaminov, S.I. Seok, M.D. McGehee, E. H. Sargent, H. Han, Challenges for commercializing perovskite solar cells, Science 361 (2018) 1214.
- [10] T.H. Han, J.W. Lee, C. Choi, S. Tan, C. Lee, Y. Zhao, Z. Dai, N.D. Marco, S.J. Lee, S. H. Bae, Y. Yuan, H.M. Lee, Y. Huang, Y. Yang, Perovskite-polymer composite cross-linker approach for highly-stable and efficient perovskite solar cells, Nat. Common. 10 (2019) 520.
- [11] S. Yang, J. Dai, Z. Yu, Y. Shao, Y. Zhou, X. Xiao, X.C. Zeng, J. Huang, Tailoring passivation molecular structures for extremely small open-circuit voltage loss in perovskite solar cells, J. Am. Chem. Soc. 141 (2019) 5781–5787.
- [12] P. Qin, G. Yang, Z. Ren, S.H. Cheung, S.K. So, L. Chen, J. Hao, J. Hou, G. Li, Stable and efficient organo-metal halide hybrid perovskite solar cells via π-conjugated lewis base polymer induced trap passivation and charge extraction, Adv. Mater. 30 (2018) 1706126.
- [13] Y. Lin, L. Shen, J. Dai, Y. Deng, Y. Wu, Y. Bai, X. Zheng, J. Wang, Y. Fang, H. Wei, W. Ma, X.C. Zeng, X. Zhan, J. Huang, π-Conjugated Lewis base: efficient trappassivation and charge-extraction for hybrid perovskite solar cells, Adv. Mater. 29 (2017) 1604545.
- [14] Y. Shao, Y. Fang, T. Li, Q. Wang, Q. Dong, Y. Deng, Y. Yuan, H. Wei, M. Wang, A. Gruverman, J. Shielda, J. Huang, Grain boundary dominated ion migration in polycrystalline organic–inorganic halide perovskite films, Energy Environ. Sci. 9 (2016) 1752–1759.
- [15] Y. Shao, Z. Xiao, C. Bi, Y. Yuan, J. Huang, Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃PbI₃ planar heterojunction solar cells, Nat. Commun. 5 (2014) 5784.
- [16] D.S. Lee, J.S. Yun, J. Kim, A.M. Soufiani, S. Chen, Y. Cho, X. Deng, J. Seidel, S. Lim, S. Huang, A.W.Y. Ho-Baillie, Passivation of grain boundaries by phenethylammonium in formamidinium-methylammonium lead halide perovskite solar cells, ACS Energy Lett. 3 (2018) 647–654.
- [17] D. Son, J. Lee, Y.J. Choi, I. Jang, S. Lee, P.J. Yoo, H. Shin, N. Ahn, M. Choi, D. Kim, N. Park, Self-formed grain boundary healing layer for highly efficient CH₃NH₃PbI₃ perovskite solar cells, Nat. Energy 1 (2016) 16081.
- [18] Q. Chen, H. Zhou, T.B. Song, S. Luo, Z. Hong, H.S. Duan, L. Dou, Y. Liu, Y. Yang, Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells, Nano Lett. 14 (2014) 4158–4163.
- [19] Z. He, J. Xiong, Q. Dai, B. Yang, J. Zhang, S. Xiao, High-performance inverted perovskite solar cells using 4-diaminomethylbenzoic as a passivant, Nanoscale 12 (2020) 6767–6775.
- [20] Y. Yang, S. Feng, M. Lid, F. Li, C. Zhang, Y. Han, L. Li, J. Yuan, L. Cao, Z. Wang, B. Sun, X. Gao, Enormously improved CH₃NH₃PbI₃ film surface for environmentally stable planar perovskite solar cells with PCE exceeding 19.9%, Nano Energy 48 (2018) 10–19.

- [21] T.P. Gujar, T. Unger, A. Schönleber, M. Fried, F. Panzer, S.V. Smaalen, A. Köhler, M. Thelakkat, The role of PbI₂ in CH₃NH₃PbI₃ perovskite stability, solar cell parameters and device degradation,, Phys. Chem. Chem. Phys. 20 (2018) 605–614.
- [22] G. Tumen-Ulzii, C. Qin, D.K.M.R. Leyden, P. Wang, M. Auffray, T. Fujihara, T. Matsushima, J.W. Lee, S.J. Lee, Y. Yang, C. Adachi, Detrimental effect of unreacted PbI₂ on the long-term stability of perovskite solar cells, Adv. Mater. (2020) 1905035.
- [23] H. Zhang, M.K. Nazeeruddin, W.C.H. Choy, Perovskite photovoltaics: the significant role of ligands in film formation, passivation, and stability, Adv. Mater. 31 (2018) 1805702.
- [24] F. Gao, Y. Zhao, X. Zhang, J. You, Recent progresses on defect passivation toward efficient perovskite solar cells, Adv. Energy Mater. 10 (2019) 1902650.
- [25] E.A. Alharbi, A.Y. Alyamani, D.J. Kubicki, A.R. Uhl, B.J. Walder, A.Q. Alanazi, J. Luo, A. Burgos-Caminal, A. Albadri, H. Albrithen, M.H. Alotaibi, J.-E. Moser, S. M. Zakeeruddin, F. Giordano, L. Emsley, M. Grätzel, Atomic-level passivation mechanism of ammonium salts enabling highly efficient perovskite solar cells, Nat. Common. 10 (2019) 3008.
- [26] Q. Wang, Y. Shao, Q. Dong, Z. Xiao, Y. Yuan, J. Huang, Large fill-factor bilayer iodine perovskite solar cells fabricated by a low-temperature solution-process, Energy Environ. Sci. 7 (2014) 2359–2365.
- [27] C.T. Lin, F.D. Rossi, J.B. Jinhyun Kim, J. Ngiam, B. Xu, S. Pont, N. Aristidou, S. A. Haque, T. Watson, M.A. McLachlan, J.R. Durrant, Evidence for surface defect passivation as the origin of the remarkable photostability of unencapsulated perovskite solar cells employing aminovaleric acid as a processing additive, J. Mater. Chem. A 7 (2019) 3006–3011.
- [28] H. Zhang, Y. Wu, C. Shen, E. Li, C. Yan, Weiwei Zhang, H. Tian, L. Han, W.-H. Zhu, Efficient and stable chemical passivation on perovskite surface via bidentate anchoring, Adv. Energy Mater. 9 (2019) 1803573.
- [29] H. Xiong, G. DeLuca, Y. Rui, B. Zhang, Y. Li, Q. Zhang, H. Wang, E. Reichmanis, Modifying perovskite films with polyvinylpyrrolidone for ambient-air-stable highly bendable solar cells, ACS Appl. Mater. Interfaces 10 (2018) 35385–35394.
- [30] D. Bi, C. Yi, J. Luo, J.D. Décoppet, F. Zhang, S.M. Zakeeruddin, X. Li, A. Hagfeldt, M. Grätzel, Polymer-templated nucleation and crystal growth of perovskite films for solar cells with effciency greater than 21%, Nat. Energy 1 (2016) 16142.
- [31] Q. Wang, Q. Dong, T. Li, A. Gruverman, J. Huang, Thin insulating tunneling contacts for efficient and water-resistant perovskite solar cells, Adv. Mater. 28 (2016) 6734–6739.
- [32] D. Bi, C. Yi, J. Luo, J.-D. Décoppet, F. Zhang, S.M. Zakeeruddin, X. Li, A. Hagfeldt, M. Grätzel, Polymer-templated nucleation and crystal growth of perovskite films for solar cells with effciency greater than 21%, Nat. Energy 1 (2016) 16142.
- [33] H. Li, C. Liang, Y. Liu, O. Zhang, J. Tong, W. Zuo, S. Xu, G. Shao, O. Cao, Covalently connecting crystal grains with polyvinylammonium carbochain backbone to suppress grain boundaries for long-term stable perovskite solar cells, ACS Appl. Mater. Interfaces 9 (2017) 6064–6071.
- [34] L. Meng, C. Sun, R. Wang, W. Huang, Z. Zhao, P. Sun, T. Huang, J. Xue, J.W. Lee, C. Zhu, Y. Huang, Y. Li, Y. Yang, Tailored phase conversion under conjugated polymer enables thermally stable perovskite solar cells with efficiency exceeding 21%, J. Am. Chem. Soc. 140 (2018) 17255–17262.
- [35] W. Chen, Y. Wang, G. Pang, C.W. Koh, A.B. Djurišic, Y. Wu, B. Tu, F. Liu, R. Chen, H.Y. Woo, X. Guo, Z. He, Conjugated polymer-assisted grainboundary passivation for efficient inverted planar perovskite solar cells, Adv. Funct. Mater. 29 (2019) 1808855.
- [36] F. Li, J. Yuan, X. Ling, Y. Zhang, Y. Yang, S.H. Cheung, C.H.Y. Ho, X. Gao, W. Ma, A universal strategy to utilize polymeric semiconductors for perovskite solar cells with enhanced efficiency and longevity, Adv. Funct. Mater. 28 (2018) 1706377.
- [37] F. Cai, J. Cai, L. Yang, W. Li, R.S. Gurney, H. Yi, A. Iraqi, D. Liu, T. Wang, Molecular engineering of conjugated polymers for efficient hole transport and defect passivation in perovskite solar cells, Nano Energy 45 (2018) 28–36.
- [38] Z. Wu, Y. Zhai, W. Yao, N. Eedugurala, Song Zhang, L. Huang, X. Gu, J.D. Azoulay, T.N. Ng, The role of dielectric screening in organic shortwave infrared photodiodes for spectroscopic image sensing, Adv. Funct. Mater. 28 (2018) 1805738.
- [39] H. Kim, Z. Wu, N. Eedugurala, J.D. Azoulay, T.N. Ng, Solution-processed phototransistors combining organic absorber and charge transporting oxide for visible to infrared light detection, ACS Appl. Mater. Interfaces 11 (2019) 36880–36885.
- [40] G. Liu, C. Zhou, F. Wan, K. Li, Y. Yuan, Y. Gao, Y. Lu, B. Yang, Dependence of power conversion properties of perovskite solar cells on operating temperature, Appl. Phys. Lett. 113 (2018) 113501.
- [41] K. Jiang, J. Wang, F. Wu, Q. Xue, Q. Yao, J. Zhang, Y. Chen, G. Zhang, Z. Zhu, H. Yan, L. Zhu, H.-L. Yip, Dopant-free organic hole-transporting material for efficient and stable inverted all-inorganic and hybrid perovskite solar cells, Adv. Mater. 32 (2020) 1908011.
- [42] Y. Zhang, C. Wu, S. Zhu, Fractionation and characterization for a propylene–ethylene random copolymer, Polym. J. 34 (2002) 700–708.
- [43] T. Suzuki, T. Sato, J. Zhang, M. Kanao, M. Higuchi, H. Maki, Electrochemically switchable photoluminescence of an anionic dye in a cationic metallosupramolecular polymer, J. Mater. Chem. C 4 (2016) 1594–1598.
- [44] M.R. Jung, F.D. Horgen, S.V. Orski, V. Rodriguez, K.L. Beers, G.H. Balazs, T. T. Jones, T.M. Work, K.C. Brignac, S.J. Royer, K.D. Hyrenbach, B.A. Jensen, J. M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, Mar. Pollut. Bull. 127 (2018) 704–716.
- [45] P. Liu, Q. Chen, S. Wu, J. Shen, S. Lin, Surface modification of cellulose membranes with zwitterionic polymers for resistance to protein adsorption and platelet adhesion, J. Member. Sci. 350 (2010) 387–394.

J. Xiong et al.

- [46] M.A. Pérez-Osorio, R.L. Milot, M.R. Filip, J.B. Patel, L.M. Herz, M.B. Johnston, F. Giustino, Vibrational properties of the organic–Inorganic halide perovskite CH₃NH₃PbI₃ from theory and experiment: factor group analysis, first-principles calculations, and low-temperature infrared spectra, J. Phys. Chem. C 119 (2015) 25703–25718.
- [47] T. Glaser, C. Müller, M. Sendner, C. Krekeler, O.E. Semonin, T.D. Hull, O. Yaffe, J. S. Owen, W. Kowalsky, A. Pucci, R. Lovrinčić, Infrared spectroscopic study of vibrational modes in methylammonium lead halide perovskites, J. Phys. Chem. Lett. 6 (2015) 2913–2918.
- [48] C.H. Chiang, M.K. Nazeeruddin, M. Gratzelc, C.G. Wu, The synergistic effect of H₂O and DMF towards stable and 20% efficiency inverted perovskite solar cells, Energy Environ. Sci. 10 (2017) 808–817.
- [49] Y. Li, L. Ji, R. Liu, C. Zhang, C.H. Mak, X. Zou, H.H. Shen, S.Y. Leuf, H.Y. Hsu, A review on morphology engineering for highly efficient and stable hybrid perovskite solar cells, J. Mater. Chem. A 6 (2018) 12842–12875.
- [50] R.D. Chavan, D. Prochowicz, B. Bończak, M.M. Tavakoli, P. Yadav, M. Fiałkowski, C.K. Hong, Gold nanoparticles functionalized with fullerene derivative as an effective interface layer for improving the efficiency and stability of planar perovskite solar cells, Adv. Mater. Interfaces (2020) 2001144. Early View.
- [51] G. Xu, R. Xue, W. Chen, J. Zhang, M. Zhang, H. Chen, C. Cui, H. Li, Y. Li, Y. Li, New strategy for two-step sequential deposition: incorporation of hydrophilic fullerene in second precursor for high-performance p-i-n planar perovskite solar cells, Adv. Energy Mater. 8 (2018) 1703054.

- [52] C. Sun, Y. Guo, B. Fang, J. Yang, B. Qin, H. Duan, Y. Chen, H. Li, H. Liu, Enhanced photovoltaic performance of perovskite solar cells using polymer P(VDF-TrFE) as a processed additive, J. Phys. Chem. C 120 (2016) 12980–12988.
- [53] J. Urieta-Mora, I. Garcia-Benito, A. Molina-Ontoria, N. Martin, Hole transporting materials for perovskite solar cells: a chemical approach, Chem. Soc. Rev. 47 (2018) 8541–8571.
- [54] R. Wu, J. Yang, J. Xiong, P. Liu, C. Zhou, H. Huang, Y. Gao, B. Yang, Efficient electron-blocking layer-free planar heterojunction perovskite solar cells with a high open-circuit voltage, Org. Electron. 26 (2015) 265–272.
- [55] T. Wang, Z. Cheng, Y. Zhou, H. Liu, W. Shen, Highly efficient and stable perovskite solar cells via bilateral passivation layers, J. Mater. Chem. A 7 (2019) 21730.
- [56] B. Hailegnaw, N.S. Saricifici, M.C. Scharber, Impedance spectroscopy of perovskite solar cells: studying the dynamics of charge carriers before and after continuous operation, Phys. Status Solidi A (2020) 200291. Early View.
- [57] J. Xiong, J. Yang, B. Yang, C. Zhou, X. Hua, H. Xie, H. Huang, Y. Gao, Efficient and stable inverted polymer solar cells using TiO₂ nanoparticles and analysized by Mott-Schottky capacitance, Org. Electron. 15 (2014) 1745–1752.
- [58] G. Tang, P. You, Q. Tai, R. Wu, F. Yan, Performance enhancement of perovskite solar cells induced by lead acetate as an additive, Solar RRL 2 (2018) 1800066.
- [59] G. Huang, C. Wang, H. Zhang, S. Xu, Q. Xu, Y. Cui, Post-healing of defects: an alternative way for passivation of carbon-based mesoscopic perovskite solar cells via hydrophobic ligand coordination, J. Mater. Chem. A 6 (2018) 2449–2455.
- [60] J. Xiong, B. Yang, C. Cao, R. Wu, Y. Huang, J. Sun, J. Zhang, C. Liu, S. Tao, Y. Gao, J. Yang, Interface degradation of perovskite solar cells and its modification using an annealing-free TiO₂ NPs layer, Org. Electron. 30 (2016) 30–35.