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1,10-Phenanthroline as an Efficient Bifunctional Passivating Agent for MAPbI₃ Perovskite Solar Cells

Ali Buyruk, Dominic Blätte, Marcella Günther, Manuel A. Scheel, Nicolai F. Hartmann, Markus Döblinger, Andreas Weis, Achim Hartschuh, Peter Müller-Buschbaum, Thomas Bein, and Tayebeh Ameri*

ABSTRACT: Passivation is one of the most promising concepts to heal defects created at the surface and grain boundaries of polycrystalline perovskite thin films, which significantly deteriorate the photovoltaic performance and stability of corresponding devices. Here, 1,10-phenanthroline, known as a bidentate chelating ligand, is implemented between the methylammonium lead iodide (MAPbI₃) film and the hole-transport layer for both passivating the lead-based surface defects (undercoordinated lead ions) and converting the excess/unreacted lead iodide (PbI₂) buried at interfaces, which is problematic for the long-term stability, into “neutralized” and beneficial species (PbI₂(1,10-phen)_x) and PbI₂(1,10-phen)_x for efficient hole transfer at the modified interface. The defect healing ability of 1,10-phenanthroline is verified with a set of complementary techniques including photoluminescence (steady-state and time-resolved), space-charge-limited current (SCLC) measurements, light intensity dependent J–V measurements, and Fourier-transform photocurrent spectroscopy (FTPS). In addition to these analytical methods, we employ advanced X-ray scattering techniques, nano-Fourier transform infrared (nano-FTIR) spectroscopy, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to further analyze the structure and chemical composition at the perovskite surface after treatment at nanoscale spatial resolution. On the basis of our experimental results, we conclude that 1,10-phenanthroline treatment induces the formation of different morphologies with distinct chemical compositions on the surface of the perovskite film such that surface defects are efficiently passivated, and excess/unreacted PbI₂ is converted into beneficial complex species at the modified interface. As a result, an improved power conversion efficiency (20.16%) and significantly more stable unencapsulated perovskite solar cells are obtained with the 1,10-phenanthroline treatment compared to the MAPbI₃ reference device (18.03%).

KEYWORDS: defects passivation, multiple ligands, 1,10-phenanthroline, lead iodide, perovskite solar cells

1. INTRODUCTION

The perovskite solar cell (PSC) technology is one of the most promising candidates to compete with the commercially available photovoltaic technologies such as crystalline silicon and copper indium gallium selenide, the dominant PV technologies on the market over the past 2 decades, due to its remarkable properties such as high device efficiency, easy solution and low-temperature processability, chemical composition tunability, and low-cost production. However, the chemical and structural properties of this material and its low-temperature processing inevitably create detrimental defects at the surface and the grain boundaries (GBs) of the perovskite polycrystalline structure, which can significantly deteriorate the photovoltaic performance and stability. For instance, the methylammonium ion (MA⁺) in MAPbI₃, which can form volatile salts, can be easily released from the 3D lattice at elevated temperature, the typical working condition of solar cells, and/or with moisture. The release of MA⁺ causes also the generation of further types of defects, such as undercoordinated Pb and Pb—I antisite defects. Trap states resulting from the MA⁺ loss are expected to form significant potential wells at the surface and grain boundaries (GBs) for charge carriers and thus lead to serious charge carrier trapping, charge accumulation, and recombination losses. Meanwhile, the presence of these defects facilitates the permeation of moisture along GBs, which again accelerates trap state formation and raises stability issues. Passivation of the defects has been developed as one of the most promising strategies to obtain an improved stability–performance balance. In this regard, different approaches have been pursued to mitigate the detrimental effects of these defects.

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57 types of materials, such as Lewis bases, Lewis acids, metal
58 cations, metal anions, alkylammonium halogenides, aromatic
59 ammonium halogenides, wide bandgap materials, hydrophobic
60 materials, and metal salts, depending on the properties and
61 functions, have been used at the interfaces of the perovskite
62 and in the bulk structure of the perovskite to heal the defects.22
63 To date, pyridine and thiophene are the only two archetype
64 Lewis bases to passivate the perovskite surface defects.24 Based
65 on the intensive study of Lewis bases, considerable progress in
66 understanding the basics and developing novel concepts has
67 been made, one of which is multiple ligand passivation. Unlike
68 the archetype monoligand passivators, this new class of Lewis-
69 base passivators contains more heteroatoms and consequently
70 more than one electron lone pair to create coordination bonds,
71 thus passivating the double- and triple-halide vacancies at the
72 surface of the perovskite.25,26 Following this approach, multiple
73 coordination bonds with the undercoordinated lead (Pb2+)
74 ions have recently been shown to significantly enhance the
75 stability of the metal–ligand complex.27
76 Importantly, the excess used PbI2 in the perovskite precursor
77 solutions aiming at better crystallization28 and passivation29
78 effects poses also some problems by changing the surface
79 electronic states and inducing traps in some cases30 as well as
80 by causing long-term stability issues.31
81 To address the points stressed above, 1,10-phenanthroline
82 (1,10-phen) is implemented as a bidentate chelating ligand
83 between the photoactive layer (MAPbI3) and the hole
84 transport layer (Spiro-OMeTAD). The 1,10-phen solution
85 with the optimized concentration of 2.5 mg mL−1 is prepared
86 from chlorobenzene (CB) and is spin-coated on the freshly
87 prepared neat MAPbI3 perovskite film at room temperature
88 without further annealing. The multiple bonding ability is
89 expected to allow 1,10-phen not only to passivate monohalide
90 and double-halide vacancies on the perovskite surface but also
91 to convert the interface buried PbI2 into beneficial complex
92 species, resulting in a more stable metal–ligand complex and a
93 remarkable improvement in the performance and stability of
94 the device.

2. RESULTS AND DISCUSSION
After the surface treatment of the reference perovskite-based
99 solar cell with the 1,10-phen small molecules, optical
100 absorption characteristics in the range of 400–800 nm are
101 mostly unaffected (Figure 1b), as would be expected for
102 the functionalization by 1,10-phen, which absorbs only in
103 the UV range below 300 nm.32 The slight enhancement of
104 UV–vis absorption in the treated film might arise from the
105 small variation in thickness and area of measurement position
106 or scattering from the top surface after treatment. To evaluate
107 the charge carrier recombination dynamics of the perovskite
108

Figure 1. (a) Schematic illustration of the perovskite crystal with representative defects and possible passivation mechanisms after the 1,10-phen surface treatment. (b) UV–vis absorption spectrum. (c) Steady-state PL spectra (excitation wavelength of 375 nm). (d) Time-resolved PL decay curves of the reference MAPbI3 and 1,10-phen-treated MAPbI films (monitored at 777 and 768 nm which were the wavelength of the maximum intensity of the steady-state photoemission of reference and treated films, respectively).
film after treatment, steady-state photoluminescence (PL) and

time-resolved PL (TRPL) measurements were performed.

The steady-state PL spectrum of the 1,10-phen-treated

perovskite film shows an over 10-fold enhanced and blue-

shifted PL compared to the MAPbI3 reference (Figure 1c),

which is a good indicator of the passivated defects and reduced

nonradiative recombination at the perovskite surface. Based on

the TRPL results, presented in Figure 1d and Table S1, the

surface passivation with 1,10-phen extends the lifetime of the

perovskite photoluminescence, on average from 77 to 225 ns,

which establishes a strong indication of suppressed trap-

assisted recombination at the surface.33 We propose that after

passivation treatment the undercoordinated lead (Pb2+) ions

can be ligand-saturated through lone pair electrons of 1,10-

phen (Figure 1a). In fact, in addition to the lead-based surface

defects, excess/unreacted lead iodide (PbI2), which are

problematic for the long-term stability, can be effectively

converted into “neutralized” and beneficial species by strong

bidentate anchoring. To prove our hypothesis and obtain more

information about the complexation tendency of lead atoms,

we first mimicked the chemical bonding of the 1,10-phen with

the undercoordinated surface lead ions and excess/unreacted

lead iodide (PbI2) by preparing model PbI2(1,10-phen) and

PbI2(1,10-phen)2 complexes34 (Figure S1) at room temper-

ature (more details are presented in the Supporting

Information). 1,10-phen and its PbI2 complex were studied

with Raman spectroscopy. After complexation of PbI2 with

1,10-phen, the typical Raman bands of PbI2 (71, 95, and 111

\( \text{cm}^{-1} \)),35 shown in Figure 2a, and the Raman signals of the

1,10-phen powder (for example, the peaks at 411, 711, 1035,

1295, and 1404 \( \text{cm}^{-1} \)), shown in Figure 2b, are retained with a

uniform upshift. Furthermore, new Raman bands are observed

for the complex at 249 and 265 \( \text{cm}^{-1} \) wavenumbers, shown in

Figure 2a with an asterisk, which is attributed to the Pb–N(1,10-phen) stretching vibrations.36–38 Indeed, these up-

shifted and observed new signals in Raman spectrum for the

complex powder are both good indicators of chemical

interactions between the small molecule ligand and Pb atoms

and support the anchoring ability of the 1,10-phen on the

unreacted PbI2 and undercoordinated lead ions of the

perovskite surface.

X-ray diffraction (XRD), grazing-incidence wide-angle X-ray

scattering (GIWAXS), and scanning electron microscopy (SEM)

measurements were used to investigate the crystallinity and

morphological properties of the reference MAPbI3 and the

1,10-phen-treated films. In the XRD patterns of the reference

film, the peak relating to the intentionally used excess PbI2

(+5\%) is prominently observed at 12.63°. In contrast, this PbI2

peak almost vanishes in the XRD pattern of the 1,10-phen-
treated film, which we attribute to the surface treatment

(Figure 2c). This is consistent with the Raman spectroscopic

results (Figure 2a,b) relating to the complexability of

1,10-phen with lead ions and excess PbI2. Furthermore, a new

peak is observed at around 9.56° in the 1,10-phen-treated film,

which can be attributed to a newly formed phase. Indeed, the

corresponding SEM images reveal the formation of additional

platelets on the surface of the perovskite film (Figure 4b) after

1,10-phen treatment. To examine the new phase formed after

the surface treatment, X-ray diffraction patterns of 1,10-phen

and its model coordination compounds with PbI2 (PbI2(1,10-

phen) and PbI2(1,10-phen)2)34 in powder forms were

evaluated (Figure 2d). The new peak observed in the 1,10-
Phen-treated film does not overlap with the pure 1,10-phen XRD patterns. However, this peak is very close to that of the PbI$_2$(1,10-phen) and PbI$_2$(1,10-phen)$_2$ peaks at 9.60$^\circ$ and 9.46$^\circ$, respectively. We attribute this feature to the presence of a combination of the two coordination compounds. Besides that, a weak peak relating to PbI$_2$(1,10-phen)$_2$ complex at around 12.53$^\circ$ is observed. It suggests the formation of mixed-complex forms ($\text{PbI}_2$($\text{1,10-phen}$)$_x$, $x = 1, 2$) after surface treatment, during which a large portion of the excess used PbI$_2$ (+5%) is reacted with 1,10-phen to form the predicted model coordination compounds.

To confirm the formation of new species on the surface of the MAPbI$_3$ film, 2D GIWAXS images were taken at various grazing-incidence angles of the pristine MAPbI$_3$ thin film and the 1,10-phen-treated film (Figures 3a,b and 3c,d, respectively). The grazing-incidence geometry allows for highly surface-sensitive measurements with an X-ray scattering depth of a few nanometers at incidence angles below the critical angle (Figure S3). Thus, it is possible to confirm the formation of new species on the surface of the MAPbI$_3$ film.
190 of new species that are predominantly present at the surface of the perovskite layer. Indexing pseudo-XRD patterns obtained by radial cuts of the 2D GIWAXS data are found in the Supporting Information (Figure S2). Two new Bragg rings appear at 0.65 and 0.76 Å\(^{-1}\) for the 1,10-phen-treated sample, which correspond to a \(d\)-spacing of 9.67 and 8.27 Å, respectively. This agrees well with the newly observed Bragg peak in the XRD measurement at 9.56°, which is attributed to the \(\text{PbI}_2(1,10\text{-phen})_x\). The highest intensity is seen at an incidence angle of around 0.15 ± 0.05° which puts the critical angle of the new species in that regime. This is well below the critical angle of the perovskite material of around 0.17° at an X-ray energy of 12.4 keV. The density of the new species can thus be estimated to be well below the density of the perovskite material. The new species is partially oriented, which is evident from the radial intensity distribution of both 

Figure 5. (a) Top-view SEM image of 1,10-phen-treated MAPbI\(_3\) perovskite recorded with secondary electrons showing the additional platelets after treatment with bright contrast. (b) Pb distribution map using Pb–M series X-rays (~2.35 keV). The darker shade of green illustrates a lower Pb content in the platelets than in MAPbI\(_3\). (c) C distribution map using C–K X-rays (~0.28 keV). The relative amount of carbon in the platelets is higher than in MAPbI\(_3\).

Figure 6. Cross-sectional STEM-HAADF image of 1,10-phen-treated MAPbI\(_3\) (obtained with FIB). A rodlike dark surface phase (yellow circle) is standing on the perovskite film. A thin layer of dark material (red rectangle) on the perovskite hints at the wetting of the perovskite by the surface phase. The dark surface phase is surrounded by layers of a protective platinum film, successively grown by electron-beam-induced (dark gray) and ion-beam-induced (coarse light gray) deposition. An EDX map of this area is shown in Figure S4.

Figure 7. HAADF-STEM image of perovskite film, rodlike surface-grown feature, and surrounding Pt layer and corresponding EDX maps of Pb, I, Pt, and C. Brighter colors indicate a higher relative elemental amount. In the surface phase, the Pb and I contents are lower than in the perovskite while the C content is higher. The energy of carbon K-alpha is close to the energy of platinum N-lines; therefore, the surrounding Pt also appears as if it would contain carbon. The nitrogen count rate is too low for a meaningful elemental map.
206 Bragg rings, showing a maximum around $\chi = 0^\circ$ and 45° for the
207 rings at 0.65 and 0.76 Å$^{-1}$, respectively (indicated by white
208 arrows in Figure 3c). The high degree of orientation agrees
209 well with the surface morphology seen in the SEM images
210 (Figure 4b) and can be attributed to oriented growth induced
211 by the MAPbI$_3$ perovskite surface.

212 Based on the SEM images analysis, the MAPbI$_3$ grain size
213 and distribution in the reference and surface-treated
214 films are similar to each other (Figure 4b) and can be attributed to oriented growth induced
215 by the MAPbI$_3$ perovskite surface.

216 Based on the SEM images analysis, the MAPbI$_3$ grain size
217 and distribution in the reference and surface-treated films are
218 similar to each other (Figure 4b). In addition, the surface of
219 the treated sample reveals the presence of new platelets with a
220 height in the 300–350 nm range (Figure S11), whose edges
221 are predominantly tilted toward the perovskite surface. Atomic

222 number sensitive backscattered electron images indicate the lower overall atomic weight of the surface phase. EDX analysis
223 by SEM reveals a strongly increased carbon content of the plates (Figure 5c), while X-rays typical for Pb, I, and N signals
224 were also observed (Figure S6). However, this top-view measurement geometry does not exclude signals from the subjacent perovskite, also containing Pb, I, and N. For further analysis of the surface phase, a cross section (prepared by focused ion beam (FIB) machining; see the Supporting Information) of the 1,10-phen-treated film was studied by atomic number sensitive HAADF-STEM (Figure S4). The dark contrast of the additional phase as compared to the

Figure 8. (a) Nano-FTIR spectra of 1,10-phen-treated MAPbI$_3$ film on a silicon wafer as well as powder forms of 1,10-phen and PbI$_2$(1,10-phen)$_2$. The inset shows 27 (B$_i$) and 49 (B$_j$) modes of 1,10-phen, arising from C–H bending vibrations of the N-containing rings and the central aromatic ring, respectively. (b) Nano-FTIR spectra of reference (untreated MAPbI$_3$) and 1,10-phen-treated films on silicon wafers as a function of nanoscale sample position. The inset shows a 2 μm × 5 μm topography scan of the treated film with the positions marked where spectra have been recorded.

Figure 9. (a) J–V characteristics and (b) EQE spectra and integrated photocurrents of the best reference and 1,10-phen treated PSC devices. (c) Chart-box presentation of PCE and (d) $V_{oc}$ of over 50 (totally) reference and 1,10-phen-treated PSC devices, conducted in five different experimental runs.

4
MAPbI$_3$ perovskite film illustrates an overall lower atomic number. In Figure 6, the platelet surface phase can be observed not only as rodlike features but also as thin-film (∼10 nm) coverage on the perovskite, hinting to wetting of the perovskite by the surface phase. EDX maps of the STEM cross-section image, shown in Figure 7, reveal the presence of C, N, Pb, and I in the rodlike features, the latter two at lower relative amounts compared to the perovskite (Figure S6).

To complement the information obtained with the above electron microscopic analyses, the recently developed nano-FTIR technique was used to elucidate the chemical structure of the treated sample with 10−20 nm spatial resolution.42,43 1,10-phen (powder), PbI$_2$ (1,10-phen)$_2$ (powder), the reference film (MAPbI$_3$ neat), and the 1,10-phen-treated film were studied separately with nano-FTIR to visualize the chemical composition of the sample surface (Figure 8a,b). First, the 1,10-phen-treated film was studied in comparison with the powder forms of 1,10-phen and PbI$_2$(1,10-phen)$_2$ (Figure 8a). The two most prominent absorption bands at 725 and 861 cm$^{-1}$ (Table S2; C−H bending vibrations of the N-containing rings and the central aromatic ring, respectively) in the 1,10-phen-treated film demonstrate the presence of the 1,10-phen molecule with mono- and bis-complex forms on top of the MAPbI$_3$. In addition, the above TEM analysis (Figure 6) gives evidence for different morphologies of 1,10-phen present depending on the sample position. To gain more insight into the local structure of the treated surface, neat perovskite (reference) and treated films were studied with the sample positions for nano-FTIR spectra recording marked in the topography image (Figure 8b, inset). For the neat perovskite (reference) and treated films, the 1280−1800 cm$^{-1}$ range was selected and studied to understand the formation of the different morphologies upon 1,10-phen treatment. The band at 1470 cm$^{-1}$ observed in the nano-FTIR spectra of both reference and 1,10-phen-treated films on silicon wafers (Figure 8b) is a well-known vibrational mode of MAPbI$_3$ (symmetric NH$_3^+$ bend).44 The 1,10-phen-treated films show additional peaks at 1493 and 1515 cm$^{-1}$ (Figure 8b, spectra A and B) which are due to vibrational IR-active modes of PbI$_2$ (1,10-phen)$_x$ ($x = 1, 2$)45 although with different relative contributions (Table S2). At position B, located on top of one of the plate-shaped formations observed in SEM and TEM measurements (Figure 8b and Figure 6, yellow circle), the PbI$_2$ (1,10-phen)$_x$ signatures are most prominent. At position A, which is a location directly over the smooth surface formed by the thinner capping layer observed in the TEM measurement (Figure 6, red rectangle), the contributions are substantially reduced. These observations in the nano-FTIR of the treated film originating from different spots verify the formation of two different morphologies with the same chemical composition.

<table>
<thead>
<tr>
<th>sample</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$J_{sc}^{a}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference (RS$^b$)</td>
<td>22.35 (22.26)</td>
<td>21.31</td>
<td>1.09 (1.03)</td>
<td>74 (57)</td>
<td>18.03 (13.07)</td>
</tr>
<tr>
<td>1,10-phen-treated (RS)</td>
<td>22.58 (22.60)</td>
<td>21.75</td>
<td>1.13 (1.11)</td>
<td>79 (66)</td>
<td>20.16 (16.56)</td>
</tr>
</tbody>
</table>

$^a$The integrated photocurrent density calculated from the EQE spectrum. $^b$RS: reverse scans.

Figure 10. (a) Dark $J$−$V$ characteristics of electron-only devices. (b) Light intensity dependent $V_{oc}$ data. (c) Fourier-transform photocurrent spectroscopy results. (d) Stability test of reference and 1,10-phen-treated devices without encapsulation.
for the 1,10-phen passivated film. Together, these observations support the notion of the formation of two distinct morphologies of PbI₂ (1,10-phen) on the surface of MAPbI₃ film with the same chemical compositions, namely as a thinner film and as relatively large plate-shaped formations.

To evaluate the surface passivating performance of 1,10-phen for MAPbI₃ under optimized conditions, an n-i-p planar heterojunction perovskite solar cell was fabricated with the following structure: glass/ITO/SnO₂/MAPbI₃/with or without 1,10-phen/spiro-OMeTAD/Au. The current density–voltage (J–V) curves of the best performance devices are presented in Figure 9a, and their corresponding performance parameters are listed in Table 1. Upon comparison with the reference cell made with MAPbI₃, the 1,10-phen surface-treated device shows higher PCE performance, mainly due to the improved Voc and fill factor (FF) (Figure 9d and Figure S7b).

The best reference device gives a PCE of 18.03%, with a Voc of 1.09 V, a Jsc of 22.35 mA cm⁻², and a fill factor (FF) of 74%. In comparison with the best reference device, the 1,10-phen surface-treated device shows a striking enhancement, a PCE of 20.16%, with a Voc of 1.13 V, a Jsc of 22.58 mA cm⁻², and fill factor (FF) of 79%. The reference device suffers from a severe hysteresis index (HI) of 0.28, while the 1,10-phen-treated device shows a decreased HI of 0.15 under the same scanning conditions. The enhanced Voc of the treated device indicates the effective passivation of surface defects and reduced trap-assisted recombination. The higher FF value for the treated device (Figure 9d) can be also related to a more efficient hole extraction at the modified interface of the highly polarized perovskite layer and the nonpolarized HTL, as will be discussed later on. The integrated photocurrent densities, calculated based on the external quantum efficiency (EQE) (Table 1), 21.31 mA cm⁻² for the reference and 21.75 mA cm⁻² for the 1,10-phen-treated device, are in line with the Jsc values from the solar simulator. The slightly higher photo-current densities in the treated device can be attributed to a more efficient hole extraction at the modified interface after defect passivation. Significantly, the average performance values of over 50 samples, fabricated at different experimental runs, show a similar trend of improvement as the champion devices (Figure 9d and Figure S7a,b).

To evaluate the surface passivation effects on trap density via the space-charge limited current (SCLC) method, electron-only devices were prepared with the device configuration of ITO/SnO₂/MAPbI₃/with or without 1,10-phen/PCBM/Au. The dark J–V characteristics of both electron-only devices, reference (without phen) and the 1,10-phen-treated one (with phen), are shown in Figure 10a. The trap-density can be calculated according to the following equation:

\[ n_i = \frac{2\varepsilon \varepsilon_0 V_{TPL}}{\varepsilon L^2} \]

where \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constants of perovskite and vacuum permittivity, respectively, \( L \) is the thickness of the perovskite films, \( \varepsilon \) is the elementary charge, and \( V_{TPL} \) is the trap-filled limit voltage. The observed linear region at low bias corresponds to the ohmic response. Above the low bias voltage, after the kink points which show filled trap states marked with black and blue circles for reference and 1,10-phen-treated electron only devices, respectively, both devices show a sudden nonlinear increase in current response corresponding to the SCLC region. The calculated trap-densities \( n_i \) of reference and 1,10-phen-treated films are 8.98 \( \times 10^{15} \) and 5.00 \( \times 10^{15} \) cm⁻³, respectively, confirming that surface passivation can lower the trap density.

To enhance the understanding of the recombination behavior in the reference cell and in the passivated one, light-intensity-dependent J–V measurements were performed. The dependence of the Voc on light intensity for the reference and the treated sample is shown in Figure 10b. According to \( V_{oc} \sim \frac{kT}{q} \ln(I) \) with the Boltzmann constant \( k \), the temperature \( T \), and the elementary charge \( e \), the ideality factor \( n \) can be calculated from the slope of \( V_{oc} \) versus the natural logarithm of the light intensity I. From the linear fits, an ideality factor of 1.54 and 1.04 is obtained for the reference cell and the treated cell, respectively. The considerably reduced ideality factor indicates that trap-assisted recombination is suppressed to a great extent by the treatment with 1,10-phen.

To gain additional insight into the effect of the passivation on defect states, the photocurrent contributed by sub-bandgap states was further analyzed. As shown by Yavari et al., these sub-bandgap states in perovskite solar cells directly relate to the defect state density. The results are shown in Figure S8, where the photocurrent signal of the 1,10-phen-treated cell is below that of the untreated cell in the sub-bandgap region above 820 nm. At wavelengths below 820 nm, the respective photocurrent is higher due to the EQE increase discussed above. Above 820 nm, only sub-bandgap states can contribute to the photocurrent. Thus, the EQE measurements imply that the 1,10-phen treatment greatly reduced the formation of defect states, thereby reducing nonradiative loss pathways and increasing the Voc and the overall device performance.

Additionally, Fourier-transform photocurrent spectroscopy (FTPS) was applied, which is very well suited to study photocurrent contributions from sub-bandgap states. The results are shown in Figure 10c. In the region from 805 to 825 nm, before the noise masks the signal, 1,10-phen-treated films showed a significantly lower photocurrent from sub-bandgap states, which agrees with the less pronounced trend observed in the EQE.

Finally, we investigated the trap-assisted nonradiative \( V_{oc} \) losses after defect passivation. The losses can be calculated from the difference of the radiative limit of the \( V_{oc} \) including only radiative losses, and the measured \( V_{oc} \):

\[ \Delta V_{oc} = V_{oc,rad} - V_{oc} \]  

The relationship of \( V_{oc,rad} \) with the currents of the solar cell, namely the photogenerated current \( J_{ph} \) and the dark saturation current density \( J_{0,rad} \), is shown as:

\[ J_{oc,rad} = \frac{kT}{q} \ln \left( \frac{J_{ph}}{J_{0,rad}} + 1 \right) \]

As established by Rau, \( J_{0} \) can be calculated from the EQE \( J_{eq,rad} = \int \text{EQE}_{EL} (E) \Phi_{BB}^*(E) dE \) and the blackbody spectrum \( \Phi_{BB} \):

\[ J_{eq,rad} = \frac{q}{\text{EQE}_{EL}} \int \text{EQE}_{PV} (E) \Phi_{BB}^*(E) dE \]

Hereby \( \text{EQE}_{EL} \) is the electroluminescence EQE, which in the case of the radiative limit is to be unity, and thus \( J_{0,rad} \) can be deducted from the \( \text{EQE}_{PV} \) measurement. Lastly, since \( \text{EQE}_{PV} \) is evaluated at short circuit, \( J_{ph} \) in the following equation becomes \( J_{oc} \) which can be calculated as the integrated current of the \( \text{EQE}_{PV} \) spectrum.
The results are shown in Table 2. Because of the exponential increase of the blackbody radiation toward longer wavelengths, the higher EQE values of the treated cell at lower wavelengths and the higher EQE values of the untreated cell in the sub-bandgap region both result in fairly similar \( J_{SC}/J_{rad} \) values. Hence, \( J_{SC} \) and \( J_{rad} \) were only marginally increased in the treated cells, which did not alter \( V_{oc,rad} \). However, because of the distinct increase of the measured \( V_{oc} \), nonradiative losses must have been substantially decreased by 50 mV due to a reduction of defect state density.

Table 2. Photovoltaic Parameters of Reference and Treated Cells for Nonradiative Loss Calculations

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_{SC} ) [mA/cm(^2)]</th>
<th>( J_{rad} ) [mA/cm(^2)]</th>
<th>( V_{oc,rad} )</th>
<th>( V_{oc,measured} )</th>
<th>( \Delta V_{oc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>21.30</td>
<td>1.48 ( \times 10^{-3} )</td>
<td>1.29</td>
<td>1.09</td>
<td>0.20</td>
</tr>
<tr>
<td>1,10-phen-treated</td>
<td>21.70</td>
<td>1.55 ( \times 10^{-3} )</td>
<td>1.29</td>
<td>1.14</td>
<td>0.15</td>
</tr>
</tbody>
</table>

To understand the impact of the newly formed \((\text{PbI}_2(1,10\text{-phen}))\) (\( x = 1, 2 \)) on the perovskite surface on charge extraction at the HTL interface and device performance, various MAPbI\(_3\) films (glass/FTO/SnO\(_2\)/MAPbI\(_3\)/with or without 1,10-phen) and \( n \)-i-\( p \) planar heterojunction perovskite solar cells (glass/FTO/SnO\(_2\)/MAPbI\(_3\)/with or without 1,10-phen/spiro-OMeTAD/Au) were prepared in the same batch with stoichiometric (no excess PbI\(_2\)) and excess PbI\(_2\) (+5%) contents for XRD measurements and solar cells studies, respectively. Importantly, the XRD results for the surface-treated perovskite films with increasing concentration of 1,10-phen solution prepared from two different solvents (chlorobenzene and toluene), shown in Figure S9, reveal that treated samples with a higher concentration of 1,10-phen in chlorobenzene solution show stronger peaks of newly formed \((\text{PbI}_2(1,10\text{-phen}))\) \( (x = 1, 2) \) accompanied by partially and completely vanished \( \text{PbI}_2 \) peaks for excess \( \text{PbI}_2 \) and stoichiometric films, respectively. The SEM top and cross-section view images of untreated (reference) and surface treated MAPbI\(_3\) perovskite films (with excess \( \text{PbI}_2 \) (+5%)) with different concentrations of 1,10-phen were also recorded to observe the surface morphological changes of the films (Figures S10 and S11). With increasing concentration of 1,10-phen solution, the surface of treated samples shows more platelet formation, which is in good agreement with the XRD results. Obviously, the excess (+5%) or untreated \( \text{PbI}_2 \) gets more and more consumed with increased concentrations of 1,10-phen. This trend confirms that \( \text{PbI}_2 \) is converted into \( \text{PbI}_2(1,10\text{-phen}) \) \((x = 1, 2)\) with the coordination of 1,10-phen. Unlike the samples treated with chlorobenzene solution of 1,10-phen, the samples treated with a toluene solution \((x = 1, 2)\) in the XRD patterns of both stoichiometric and excess PbI\(_2\) films. These different results can be attributed to the solubility of 1,10-phen (monohydrate and anhydrate forms) in chlorobenzene and toluene. Perovskite solar cell devices prepared under the same conditions as the XRD samples were analyzed to understand the effects of the additional new lead complexes on the device performance as a result of the reaction of excess/unreacted lead iodide (\( \text{PbI}_2 \)) with 1,10-phen (Figure S12). On the one hand, solar cell devices treated in the toluene solution in which new complex species are not observed show enhancements that result from higher \( V_{oc} \) and fill factor (FF), which can be attributed to 1,10-phen-saturated undercoordinated lead (\( \text{Pb}^{2+} \)) ions on the surface. On the other hand, in the case of the treatment of the \( \text{PbI}_2 \) excess MAPbI\(_3\) devices with a chlorobenzene solution of the passivation agent, the devices show not only doubled enhancement in \( V_{oc} \) and fill factor (FF) but also higher \( J_{SC} \) which shows the beneficial effects of the defect passivation and complex formation on the perovskite surface on charge extraction and device performance.

To further solidify this hypothesis, samples were fabricated with the following structure: glass/MAPbI\(_3\)/with or without 1,10-phen/spiro-OMeTAD to evaluate the impact of the new surface species (Figure 4b) at the interface of MAPbI\(_3\)/spiro-OMeTAD on the interfacial charge transfer dynamics and studied with steady-state photoluminescence (PL) (Figure S13) and time-resolved PL (TRPL) (Figure S14) measurements. The treated (with 1,10-phen) sample showed notable quenching of the steady-state photoluminescence, indicating accelerated carrier extraction at the modified MAPbI\(_3\)/spiro-OMeTAD interface and contributing to the enhanced FF and \( J_{SC} \) in device performance (Figure S7a,b). With regard to the time-resolved PL (TRPL) measurements, the decrease (from 470 to 8 ns) in the fast component \((t_f)\) of the decay lifetime of the treated sample with higher fractional amplitude supports the observed notable quenching of the treated sample in the steady-state photoluminescence measurements. All these quenching experiments show that the treated interface transfers the photogenerated holes from perovskite to spiro-OMeTAD faster than the neat perovskite (without 1,10-phen).

And finally, regarding the DFT-calculated HOMO (highest occupied molecular orbital) energy levels (Figure S15) of model \( \text{PbI}_2(1,10\text{-phen}) \) \((\sim 5.04 \text{ eV})\) and \( \text{PbI}_2(1,10\text{-phen}) \) \((\sim 4.69 \text{ eV})\) complexes, which are consistent with the energy level calculations of \( \text{PbI}_2(dmp) \) \((\sim 5.30 \text{ eV})\) (a complex very similar to \( \text{PbI}_2(1,10\text{-phen}) \)), one of them perfectly matches the related energy levels of spiro-OMeTAD (HOMO, \(-4.90 \text{ eV})\) and MAPbI\(_3\) (valence band edge, \(-5.30 \text{ eV})\), leading a favorable cascade band alignment (Figure S16) for more efficient hole transfer at the modified interface.

To assess the stability of the devices, the performances of the unencapsulated passivated and reference devices were tracked under the conditions of a relative humidity of 40–45% at room temperature. As shown in Figure 10d, the 1,10-phen-treated and the reference devices retain 94% and 74% of starting PCE after 30 days (720 h), respectively. To understand the impact of the 1,10-phen treatment on the surface hydrophobicity, the water contact angles of bare perovskite (reference) and 1,10-phen-treated films were measured. As shown in Figure S17, the bare perovskite and the treated film exhibit a water contact angle of around 61° and 73°, respectively. The greater water contact angle of the treated film compared to the reference shows the enhanced hydrophobicity of the treated surface. In addition to the shelf-stability test, explained above, the performance of the unencapsulated passivated and reference devices was tracked under continuous 1-sun illumination with a fixed temperature of 60 °C for 12 h in the glovebox to evaluate light thermal stability (Figure S18). Under these conditions, the treated and reference devices retain 75% and 50% of their starting PCE, respectively. These results establish that the defect passivation upon 1,10-phen surface treatment and converting excess/unreacted lead iodide (\( \text{PbI}_2 \)) into

\[
I_{EC} = q \int \text{EQE}\text{PV}(E)\Phi_{AML}\text{Sg}(E) \, dE \tag{4}
\]
“neutralized” and beneficial species \((\text{PbI}_2(1,10\text{-phen})_x \times = 1, 2)\) impact not only the device performance but also the device stability, which will be of particular importance toward the application of perovskite solar cells.

3. CONCLUSION

In summary, we have successfully implemented 1,10-phenanthroline, known as a bidentate chelating ligand, first to heal detrimental defects on MAPbI\(_3\) surfaces, which adversely affect the photovoltaic performance and stability of corresponding devices, and second to convert excess or unreacted PbI\(_2\), which is also detrimental for the long-term stability of solar cell devices, into beneficial species \((\text{PbI}_2(1,10-\text{phen})_x \times = 1, 2)\) for efficient hole transfer at the modified interface. Combining the nano-Fourier transform infrared (nano-FTIR) spectroscopy and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) techniques, we confirmed surface coverage of the treated films with PbI\(_2(1,10\text{-phen})_x\) which is found to form two different morphologies as either a platelet-shaped formation or a very thin capping layer with the same chemical composition. As a result, the 1,10-phen surface-treated devices show over 10% performance improvements demonstrated by the champion PCE of 20.16%, with a \(V_{OC}\) of 1.13 V, a \(J_{SC}\) of 22.58 mA cm\(^{-2}\), and a fill factor (FF) of 79%. We attribute these substantial improvements to passivation of the monohalide and double-halide vacancy defects (undercoordinated lead ions) at the surface of the perovskite, which cause nonradiative recombination and voltage losses, and of excess/unreacted lead iodide \((\text{PbI}_2)\), which are problematic for the long-term stability of the PSCs. Moreover, under the conditions of a relative humidity of 45% at room temperature, the unencapsulated passivated device showed significantly higher stability compared to the untreated reference device.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c05055.

XRD studies, pseudo-XRD studies integrated with 2D GIWAXS, X-ray scattering depth analysis, STEM-HAADF image with EDX compositional map, device optimizations, SEM top and cross-section view images, PL quenching experiments, DFT calculations, contact angle measurements, additional stability test, time-resolved photoluminescence decay components, IR-active vibrational bands of related complexes and synthesis (PDF).

**AUTHOR INFORMATION**

**Corresponding Author**

Tayebeh Ameri — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany; Institute for Materials and Processes, Chemical Engineering, University of Edinburgh, EH9 3FB Edinburgh, U.K.; orcid.org/0000-0002-8928-3697; Email: tayebeh.ameri@ed.ac.uk

**Authors**

Ali Buyruk — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Dominic Blätte — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Marcella Günther — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany; orcid.org/0000-0002-5624-6785

Manuel A. Scheel — Lehrstuhl fuumlr Funktionelle Materialien, Physik-Department, Technische Universität Muumlnchen, 85748 Garching, Germany; orcid.org/0000-0003-0508-6694

Nicolai F. Hartmann — AttoCore Systems AG, D-85540 Haar, Germany

Markus Döblinger — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Andreas Weis — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Achim Hartschuh — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany

Peter Müller-Buschbaum — Lehrstuhl fuumlr Funktionelle Materialien, Physik-Department, Technische Universität Muumlnchen, 85748 Garching, Germany; Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, 85748 Garching, Germany; orcid.org/0000-0002-9566-6088

Thomas Bein — Department of Chemistry and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, 81377 Munich, Germany; orcid.org/0000-0001-7248-5906

**Notes**

The authors declare no competing financial interest.

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