Dependence of material properties and photovoltaic performance of triple cation tin perovskites on the iodide to bromide ratio

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Abstract

In this work, the influence of a partial introduction of bromide ($x=0-0.33$) into $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ (MA: methylammonium, FA: formamidinium, PEA: phenylethylammonium) triple cation tin perovskite on the material properties and photovoltaic performance is investigated and characterized. The introduction of bromide shifts the optical band gap of the perovskite films from 1.29 eV for the iodide-based perovskite to 1.50 eV for the perovskite with a bromide content of $x=0.33$. X-ray diffraction measurements reveal that the size of the unit cell is also gradually reduced based on the incorporation of bromide. Regarding the photovoltaic performance of the perovskite films, it is shown that already small amounts of bromide ($x=0.08$) in the perovskite system increase the open circuit voltage, short circuit current density and fill factor. The maximum power conversion efficiency of 4.63% was obtained with a bromide content of $x=0.25$, which can be ascribed to the formation of homogeneous thin films in combination with higher values of the open circuit voltage. Upon introduction of a higher amount of bromide ($x=0.33$), the perovskite absorber layers form pinholes, thus reducing the overall device performance.

Graphic abstract

Keywords Material science · Solar cell · Lead-free perovskite · Semiconductors

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Introduction

Intensive studies on lead halide perovskites within the past years have shown their great potential as absorber materials in photovoltaics. Lead halide perovskite solar cells are exhibiting high power conversion efficiencies (PCEs) up to 24.2% and are already catching up with conventional thin film solar cell technologies, such as CdTe or CIGS in terms of efficiency [1, 2]. Nevertheless, the toxicity of lead itself, in particular, affiliated with the good solubility of lead halide species in water is one of the biggest hindrances for a swift commercialization [3]. Therefore, there is a growing endeavor to substitute lead with alternative elements showing less toxicity but similar properties to lead [4, 5].

The most promising among these elements is tin due to its similar electronic structure and ionic radius to lead (Pb^{2+} : 119 pm; Sn^{2+} : 110 pm) [6].

In 2014, the first studies on tin perovskite solar cells in n-i-p device architecture with perovskites based on methylammonium (MA^+) as A-cation, have been reported, already showing PCEs of 5–6% [7–9]. However, a major drawback for tin perovskite solar cells is the easy oxidation of Sn^{2+} to Sn^{4+} in the presence of oxygen which leads to a self p-doping. The standard redox potentials for tin (E_0 of $\text{Sn}^{2+}/\text{Sn}^{4+} = +0.15$ V) and lead (E_0 of $\text{Pb}^{2+}/\text{Pb}^{4+} = +1.67$ V) indicate that Sn^{2+} is thermodynamically less favorable compared to Pb^{2+} which corroborates the sensitivity of Sn^{2+} towards oxidation [10]. One common approach to reduce the oxidation of Sn^{2+} is the use of SnF_2 as reducing agent. Several research groups investigated different SnF_2 concentrations and found that approximately 10 mol% of the reducing agent is ideal to improve the perovskite film formation and also the power conversion efficiency [11–13]. Gupta et al. recently highlighted several possible effects of SnF_2 on the solar cell properties [10], however, the role of SnF_2 in these devices is still not fully elucidated. Song et al. demonstrated that hydrazine vapor during the perovskite deposition can further diminish the Sn^{4+} concentration and also lower the defect concentration [14].

In the last years, tin perovskites with various compositions were investigated and efficiencies up to 9.6% have been obtained [13, 15, 16]. Jokar et al. realized pinhole-free FASnI_3 (FA: formamidinium) perovskite thin films by the addition of 1% ethylenediammonium diiodide (enI_2), reaching a maximum efficiency of 8.9% in the corresponding solar cells [17]. In a further step, the incorporation of 20% guanidinium (GA^+) into the ($\text{FASnI}_3 + 1\% \text{enI}_2$) perovskite resulted in the current record power conversion efficiency of 9.6% (8.3% certified) for tin perovskite solar cells [16]. On the other hand, Wang et al. fabricated 2D-quasi-2D–3D tin perovskite solar cells based on $\text{PEA}_{0.15}\text{FA}_{0.85}\text{SnI}_3$ (PEA: phenylethylammonium) and used NH_4SCN to tailor the tin perovskite structure and reached efficiencies of 9.41% [18].

This introduction of large A-cations in the perovskite lattice such as PEA^+ became attractive to form 2D/3D perovskites [11, 15]. Bigger cations are able to break up the 3D structure to form mixed 2D/3D crystal structures. Thereby the perovskites gain higher stability, which is ascribed to the hydrophobic character of these cations [19]. In other reports, the authors claim that the PEA A-cation is able to block oxygen diffusion paths making the perovskite less sensible against degradation and, furthermore, a reduction of background carrier density was found, which improves the carrier transport due to longer lifetime of the respective charge carriers [11, 15]. Promising solar cells with FA and PEA ions have already been fabricated and efficiencies of 5.94% [11] and 9.0% [15] were obtained. In our previous

study, we have shown that solar cells with the triple cation perovskite $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{SnI}_3$ exhibit an excellent shelf life of more than 5000 h and also remarkable stability under operation [20].

An alternative method for tailoring the perovskite absorber layer is the introduction of smaller X-anions [9, 21–25]. In an early study on lead-free tin perovskites, Hao et al. already investigated the substitution of iodide with bromide in $\text{MASnI}_{3-x}\text{Br}_x$ perovskite solar cells [9]. The wider optical band gap due to the introduction of bromide led to an increase in open circuit voltage and overall better device performance. When using $\text{CsSnI}_{3-x}\text{Br}_x$ as perovskite material, in addition to the expected changes in the optical characteristics, a change in the crystal structure from orthorhombic to cubic was also observed [22]. Later, Lee et al. reported that the introduction of bromide in FASnI_3 perovskite solar cells increases the perovskite stability as well as the recombination lifetime and by using an n-i-p device architecture, a maximum PCE of 5.5% with 25% bromide in the perovskite absorber was reached [21].

In this study, $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ ($x = 0, 0.08, 0.17, 0.25, 0.33$) perovskite films are investigated and solar cells using a p-i-n planar device setup were fabricated and characterized. The perovskite films were analyzed by optical spectroscopy and X-ray diffraction to substantiate the introduction of bromide into the crystal structure. Moreover, the surface morphology and layer thicknesses were investigated by scanning electron microscopy (SEM) and surface profilometry, respectively. The tin perovskite films were applied in solar cells with the device structure glass/ITO/PEDOT:PSS/perovskite/ $\text{PC}_{60}\text{BM}/\text{Al}$, which were analyzed in terms of J – V characteristics, power output at the maximum power point (MPP tracking), hysteresis properties and external quantum efficiency (EQE).

Results and discussion

Perovskite films with the composition $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$, whereby x was set to 0, 0.08, 0.17, 0.25, and 0.33, were fabricated by dissolving the respective amounts of iodide and bromide salts in DMSO/DMF (4/1 vol%) followed by a one-step solution process using anti-solvent treatment to initiate the perovskite crystallization. For simplicity, the perovskite compositions are labeled according to their bromide content (e.g., $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_{0.25}\text{I}_{0.75})_3$ is labeled as $x = 0.25$). The fast crystallization of tin perovskites when using the anti-solvent dripping method is a major challenge in the fabrication of efficient solar cells. Therefore, a solvent ratio of DMF/DMSO (4/1 vol%) was chosen to slow down the crystallization process during spin coating through the formation of a $\text{SnI}_2 \cdot 3\text{DMSO}$ intermediate state [26]. Wu et al.

have shown that DMSO can also retard the crystallization in lead perovskite solar cells [27]. Liu et al. reported that bigger perovskite grains can be observed when DMSO is present during the annealing procedure thus leading to more homogenous films and less pinholes [28].

Optical properties

Figure 1a shows the UV/Vis absorption spectra of $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ thin films with layer thicknesses of 220, 200, 180, 175, and 170 nm for $x=0, 0.08, 0.17, 0.25$, and 0.33 , respectively. The films were prepared by the same deposition parameters as used for the solar cell fabrication. In the graph (Fig. 1a), a clear blue shift of the absorption onset with increasing bromide content of the perovskite films can be observed. The absorption onset changes from approximately 1000 nm ($x=0$) to approximately 835 nm for the composition with the highest bromide content ($x=0.33$), correlating well with other reports [9, 21]. The corresponding band gaps were determined using

Tauc plots (Fig. S1). Herein, direct transitions were found with band gap values of 1.29 eV, 1.32 eV, 1.38 eV, 1.45 eV, and 1.50 eV for the absorber layers with $x=0, 0.08, 0.17, 0.25$, and 0.33 , respectively. By plotting these values versus the bromide content, a linear correlation ($R^2: 0.981$) can be observed (Fig. 1b).

Crystallographic properties

To further investigate the introduction of bromide into the crystal lattice, X-ray diffraction patterns were recorded (Fig. 2a). The diffractograms show two distinct peaks at approx. 14° and 28° 2θ which can be assigned to the 100 and 200 peaks of a typical diffraction pattern for a mixed 2D/3D tin perovskite with quasi-cubic/orthorhombic crystal structure [11, 15, 19]. The very pronounced 100 and 200 peaks indicate a preferred orientation of the (h00) planes of the perovskite crystals parallel to the substrate. Upon the introduction of bromide, no change in the crystal structure or the preferred orientation is noticed.

Fig. 1 **a** UV/Vis absorption spectra of $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ ($x=0-0.33$) thin films deposited on glass/PEDOT:PSS substrates; **b** band gap values plotted as a function of the bromide content

Fig. 2 X-ray diffraction patterns of $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ ($x=0-0.33$) thin films prepared on glass substrates showing **a** the whole patterns and **b** a zoom in between 13.5 and 15.0° 2θ to illus-

trate the shift of the 100 peak with increasing bromide content. The diffraction patterns are shifted vertically for better visibility. **c** The lattice constants plotted as a function of the bromide content

However, all peaks gradually shift to higher diffraction angles with increasing bromide content of the samples ($x=0$ to $x=0.33$), as can be clearly seen in Fig. 2b for the 100 reflex and in Fig. S2 for the 200 reflex. This indicates a decrease in the size of the unit cell due to the incorporation of bromide instead of the larger iodide ions. The peak positions and corresponding d values of all the samples are summarized in Table S1. As observed in the case of the optical data, the quasi-cubic lattice constant a also exhibits a linear correlation (R^2 : 0.996) with the bromide content and decreases from $a = 6.250$ Å for $x=0$ to $a = 6.152$ Å for $x=0.33$ (Fig. 2c). This is in accordance with Vegard's law [29], and similar linear correlations have been also observed, e.g., for mixed halide lead or antimony perovskites [30–33].

Film morphology and solar cells

In the next step, we investigated the morphology of the perovskite films by recording top-view SEM images (Fig. 3, Fig. S3). The films with a bromide content of $x=0$ to $x=0.25$ display full coverage without any pinholes. In particular, the films with a bromide content of $x=0.17$ and $x=0.25$ appear to be very flat and show low roughness. However, by further increasing the bromide content to $x=0.33$, the perovskite film exhibits pinholes.

Furthermore, solar cells with the device structure glass/ITO/PEDOT:PSS/perovskite/PCBM/Al were fabricated (Fig. 4a). J – V curves of typical solar cells measured in backward scan direction are presented in Fig. 4b and their characteristic parameters are shown in Table 1. All measurements

Fig. 3 Top-view SEM images of $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{BrI}_{1-x})_3$ ($x=0$ – 0.33) perovskite thin films deposited on glass/ITO/PEDOT:PSS; **a** $x=0$, **b** $x=0.08$, **c** $x=0.17$, **d** $x=0.25$, **e** $x=0.33$

Fig. 4 **a** Schematic of the used solar cell architecture. **b** J – V curves of typical tin perovskite solar cells ($x=0$ – 0.33) measured in backward scan direction using an illumination mask. **c** EQE spectra of the corresponding solar cells ($x=0$ – 0.33)

Table 1 Solar cell characteristics of tin perovskite solar cells for $x=0$ –0.33 showing the best and average (best ten solar cells) values including the standard deviations

Samples	V_{OC}/V	$J_{SC}/\text{mA}/\text{cm}^2$	FF/%	PCE/%
$x=0$				
Average	0.37 ± 0.01	13.50 ± 0.77	55.3 ± 1.0	2.70 ± 0.18
Best	0.39	14.57	57.1	2.97
$x=0.08$				
Average	0.43 ± 0.01	17.12 ± 0.56	67.2 ± 1.7	3.98 ± 0.25
Best	0.44	18.10	69.6	4.52
$x=0.17$				
Average	0.45 ± 0.01	15.65 ± 2.05	64.1 ± 1.0	3.93 ± 0.16
Best	0.46	18.48	65.8	4.15
$x=0.25$				
Average	0.48 ± 0.01	15.19 ± 0.94	61.5 ± 1.0	3.88 ± 0.31
Best	0.49	16.45	63.3	4.63
$x=0.33$				
Average	0.49 ± 0.02	11.58 ± 0.91	56.0 ± 1.0	2.99 ± 0.23
Best	0.51	13.06	58.8	3.34

The measurements were acquired 1 day after fabrication

were recorded using a shadow mask (area of 0.07 cm^2) for the illumination.

As expected, the V_{OC} of the solar cells increases with the introduction of bromide into the perovskite absorber layer from 0.37 to 0.49 V because of the widening of the band gap with higher bromide content. However, a higher band gap typically leads to a lower current density due to the narrower absorption range. In contrast to that, we observed that slight amounts of bromide ($x=0.08$ –0.25) have a positive effect on the current density of the solar cells. This can be ascribed to the reduced roughness of the perovskite films and thereby an improved interface between absorber and electron transport layer. Moreover, based on previous studies on related tin perovskite materials, an improved electron extraction due to a raised conduction band of the perovskite absorber based on the incorporation of bromide is expected [9, 21]. In addition, reduced defect concentrations have been found by Lee et al. for mixed iodide/bromide formamidinium tin halide perovskite films [21].

The solar cells based on perovskites with a bromide content of $x=0$ showed an efficiency of 2.97%. The PCE is lower compared to previously published values for solar cells with a $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{SnI}_3$ absorber layer [20]. This originates from an intended simplification of the solar cell fabrication process by omitting an additional purification of the SnI_2 precursor and applying a single anti-solvent dripping instead of the two-step anti-solvent dripping procedure. Already little amounts of bromide ($x=0.08$ and $x=0.17$) have increased the efficiency, showing maximum PCEs of 4.52% and 4.15%, respectively. The highest PCE of

4.63% was reached with a solar cell comprising a tin perovskite absorber layer with a bromide content of $x=0.25$. This solar cell showed a V_{OC} of 0.49 V, a J_{SC} of $16.45 \text{ mA}/\text{cm}^2$ and a FF of 63.3%. Further increasing the bromide content to $x=0.33$ decreases the efficiency of the solar cells and PCEs of up to 3.34% were obtained. This reduced PCE originates most likely from the pinholes in the perovskite layer leading to partial short circuiting of the device. Generally, all fabricated perovskite solar cells display high reproducibility, indicated by the low standard deviations for an average of the best ten devices (see Table 1 and Fig. S4).

To investigate the hysteresis behavior, J – V curves in forward scan direction were also recorded. The corresponding light as well as dark measurements of the five perovskite compositions ($x=0$ –0.33) are given in Fig. S5 with their solar cell characteristics summarized in Table S2. A slight hysteresis was observed for the pure iodide perovskite solar cell ($x=0$), whereas the devices fabricated with $x=0.08$ –0.25 are almost hysteresis free. Upon further increasing the bromide content, a large hysteresis is observed, indicated by a change in open circuit voltage, which can be ascribed to the pinholes in the perovskite films with a bromide content of $x=0.33$ as observed in the SEM images (Fig. 3 and Fig. S3).

In addition, maximum power point (MPP) tracking measurements were performed (Fig. S6). Hereby power outputs of approximately 4.0%, 4.3%, 4.4%, 5.0%, and 3.0% were recorded for the solar cells prepared with different bromide contents $x=0$ –0.33. These PCE values are slightly higher compared to the ones extracted from the J – V curves, which is due to a light soaking effect. However, in the MPP tracking measurements, the solar cell with a bromide content of $x=0.25$ also showed the highest PCE of slightly above 5%. Moreover, it is interesting to mention that the device with the pure iodide compound $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{SnI}_3$ as absorber layer showed the most pronounced increase in PCE between initial J – V characterisation and MPP tracking.

The external quantum efficiency spectra (Fig. 4c) nicely show that the onset of photocurrent generation shifts to lower wavelengths for the solar cells prepared with higher bromide content in the absorber layers. While the onset of the EQE spectrum of the pure iodide compound is already at 1000 nm, the onset of photocurrent generation of the solar cells comprising an absorber layer with a bromide content of $x=0.33$ is at approx. 840 nm. This also matches well with the onset of the optical absorption spectra (Fig. 1a). Furthermore, the enhanced photocurrent of the solar cells fabricated with the compositions $x=0.08$ to 0.25 compared to the pure iodide ($x=0$) compound is also reflected in the EQE spectra. While the maximum EQE values for the device with the pure iodide tin perovskite absorber layer are at 55%, these values increased to 62–65% for the solar cells based on the perovskite absorbers with a bromide content of $x=0.08$ –0.25.

Conclusion

The substitution of iodide with bromide in $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ perovskite ($x=0\text{--}0.33$) led to an increase in the optical band gap from 1.29 eV to 1.50 eV for $x=0\text{--}0.33$, respectively. X-ray diffraction patterns indicate the bromide introduction by a shift of the diffraction peaks towards higher angles due to a compaction of the unit cell. Both the optical band gap and the lattice constants show a linear dependence on the bromide content. Thus, in this regard, the herein presented Sn analogues behave very similar to other perovskite systems, e.g., based on lead halides [32, 33] or antimony halides [31]. The $J\text{--}V$ characteristics of the fabricated perovskite solar cells with $x=0\text{--}0.33$ revealed an increase in V_{OC} from 0.37 to 0.49 V as expected due to the increase in the optical band gap. A maximum PCE of 4.63% was reached for the solar cells with a bromide content of $x=0.25$ in the perovskite absorber layer.

The increased performance of the perovskite solar cells caused by the addition of bromide can be related to a combination of higher open circuit voltages and the formation of more homogeneous thin films as observed in the SEM images. A further increase in the bromide content leads to obvious pinholes in the perovskite films resulting in lower device performance and pronounced hysteresis.

Thus, the introduction of bromide does not only influence the optical and structural parameters but also the crystallization and film formation. To obtain high-performance perovskite solar cells, a thorough understanding of the crystallization kinetics during thin film formation is of high importance and will be the topic of further research.

Experimental

All chemicals and solvents were used as purchased without further purification unless otherwise noted. The solvents dimethylformamide (DMF), dimethylsulfoxide (DMSO), and chlorobenzene (CB) were dried using molecular sieves (Carl Roth, 3 Å type 562 C). PEDOT:PSS was purchased from Heraeus (CLEVIOS™ P VP AI 4083), [6,6]-Phenyl C_{61} butyric acid methyl ester (PC_{60}BM) from Solenne, phenylethylammonium iodide (PEAI) from GreatCell Solar, and aluminum from Kurt J. Lesker Company. All the other chemicals were purchased from Sigma-Aldrich.

Thin film and solar cell fabrication

Patterned glass/ITO substrates ($15 \times 15 \times 1.1$ mm) with a sheet resistance of $15 \Omega/\text{sq}$ (Luminescence Technology

Corp.) were pre-cleaned with deionized water and acetone, put in an isopropyl alcohol bath, and placed into an ultrasonic bath at 40°C for 30 min. The substrates were then dried with N_2 and further plasma etched for 3 min (FEMTO, Diener Electronic). PEDOT:PSS (used as purchased) was filtered through a $0.45 \mu\text{m}$ PVDF filter, then deposited by spin coating at 3000 rpm for 60 s followed by annealing at 120°C for 20 min. For the annealing step, the substrates were transferred into a N_2 -filled glove box.

The perovskite precursor solution (1 M) was prepared by dissolving the corresponding amounts of MAI, MABr, FAI, PEAi, SnI_2 , and SnBr_2 in DMF/DMSO (4/1 vol%) to obtain the theoretical composition $\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ ($x=0, 0.08, 0.17, 0.25, 0.33$). In Table S3, the corresponding amounts used of each substance to obtain the respective compositions are given. Additionally, 10 mol% SnF_2 was added to the solutions. It should be noted that SnI_2 (and all the other precursors) was used as purchased, which is in contrast to our previous study [20], where SnI_2 was additionally purified based on different boiling points of SnI_2 and SnI_4 to keep SnI_4 impurities as low as possible. The precursor solutions were stirred overnight at room temperature under nitrogen atmosphere, followed by filtration through a $0.45 \mu\text{m}$ PTFE filter. For the preparation of the perovskite films, the respective precursor solution was spin coated on the glass/ITO/PEDOT:PSS substrates at 5000 rpm for 60 s. After 30 s, 100 mm^3 of CB were dropped on the spinning substrates (distance between tip and substrate: 1 cm) to crystallize the perovskite, indicated by color change from yellow to black. The perovskite films were then annealed at 70°C for 20 min. The electron transport layer— PC_{60}BM ($20 \text{ mg}/\text{cm}^3$ in CB)—was stirred overnight at room temperature under inert conditions and filtered through a $0.45 \mu\text{m}$ PTFE filter before use. The solution was spin coated at 6000 rpm for 60 s. Afterwards, the top electrode (100 nm Al) was deposited by thermal evaporation under high vacuum conditions ($< 1 \times 10^{-5}$ mbar) using a shadow mask (active area of 0.09 cm^2).

Characterization

$\text{MA}_{0.75}\text{FA}_{0.15}\text{PEA}_{0.1}\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ perovskite thin films were characterized by X-ray diffraction (XRD) with a PANalytical Empyrean system, which uses Cu K_α radiation. UV/Vis absorption measurements of the perovskites were performed on a Perkin Elmer Lambda 35 UV/Vis spectrometer equipped with an integrating sphere. The optical data were recorded in the wavelength range of 300–1100 nm.

Top-view SEM images of the perovskite layers prepared on glass/ITO/PEDOT:PSS substrates were acquired on a Zeiss Supra 40 scanning electron microscope with an in-lens detector and 5 kV acceleration voltage. Surface profilometry measurements were performed on a Bruker DektakXT stylus

surface profiling system equipped with a 12.5 μm -radius stylus tip. Line scans were recorded over a length of 1000 μm , with a stylus force of 3 mg, and a resolution of 0.33 $\mu\text{m}/\text{pt}$. The layer thicknesses were determined from two-dimensional surface profiles using Vision 64 software (Bruker).

J – V curves of all devices were recorded inside a glove box (nitrogen atmosphere) with a scan rate of 100 mV/s using a Keithley 2400 source meter connected to a LabView-based software. Illumination (100 mW/cm²) was provided by a Dedolight DLH400 lamp, calibrated using a monocrystalline silicon WPVS reference solar cell Fraunhofer ISE. External quantum efficiency (EQE) spectra were acquired in inert atmosphere using a MuLTImode 4-AT monochromator (Amko) equipped with a 75 W xenon lamp (LPS 210-U, Amko), a lock-in amplifier (Stanford Research Systems, Model SR830), and a Keithley 2400 source meter. The monochromatic light was chopped at a frequency of 30 Hz and constant background illumination was provided by white light LEDs. The EQE spectra were measured in the wavelength range of 380–1000 nm (increment: 10 nm). The measurement setup was spectrally calibrated with a silicon photodiode (Newport Corporation, 818-UV/DB).

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