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Thierry Pauporté, Liam Gollino, Nicolas Mercier. Iodoethylammonium (IEA⁺)-based lead- and iodide-deficient halide perovskites (d-HPs) for solar cells. Proceedings of SPIE, the International Society for Optical Engineering, 2023, Oxide-based Materials and Devices XIV., 12422, pp.52. 10.1117/12.2647859 . hal-04263771

HAL Id: hal-04263771

<https://cnrs.hal.science/hal-04263771v1>

Submitted on 29 Oct 2023

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Iodoethylammonium (IEA⁺)-based lead- and iodide- deficient halide perovskites (d-HPs) for solar cells

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ABSTRACT

Perovskite materials, despite displaying remarkable properties, suffer from the use of toxic lead and poor stability towards moisture and thermal stresses. These strongly hinder their future development. Recently, a new family of 3D perovskites, deficient in lead and iodide, the d-HPs, has been discovered. They involve large organic cations that circumvent the Goldschmidt tolerance factor. In the present study, we report that a new cation, the iodoethylammonium I-(CH₂)₂-NH₃⁺ (IEA⁺), allows the synthesis of d-HP thin films based on the 3D MAPbI₃ perovskite. This new compound has been tested for solar cell application. A final power conversion efficiency of 9.54 % was achieved.

Keywords: Perovskite solar cells, Lead- and iodide-Deficient perovskite, Iodoethylammonium, MAPbI₃, toxicity

1. INTRODUCTION

Hybrid halide perovskites (PVK) are promising semiconductors studied for numerous applications due to their various interesting optoelectronic properties such as high charge carrier mobility, tunable bandgap, high absorption coefficient, long carriers diffusion lengths and low recombination losses¹⁻⁶. Their possible applications encompass notably lasers⁷, LEDs⁸, photodetectors^{9,10} scintillation¹¹ and perovskite solar cells (PSCs)¹²⁻¹⁷. PSCs have become more and more attractive and investigated, with nowadays a record power conversion efficiency (PCE) of 25.7%¹⁸ that competes directly with the commercialized silicon photovoltaic solar cells¹⁹. Nevertheless, perovskites faces two major issues: a rather poor stability^{20,21} as well as a high toxicity caused by the presence of lead^{22,23}. To solve them, one method is to replace lead totally or partially by other elements²⁴⁻²⁶. In recent years, we reported the d-HPs (Lead -and iodide-Deficient Halide Perovskites), a new family of 3D perovskites with an original structure presenting PbI⁺ vacancies inside the perovskite lattice caused by the insertion of large organic cations that do not respect the Goldschmidt tolerance factor. Two large organic cations have been reported so far: hydroxyethylammonium, HO-(CH₂)₂-NH₃⁺ (noted HEA⁺)²⁷ and thioethylammonium, HS-(CH₂)₂-NH₃⁺ (noted TEA⁺)²⁸. By inserting these cations, lead- and iodide- deficient MAPbI₃ (MAPI) and FAPbI₃ (FAPI) have been obtained with 3D corner-shared Pb_{1-x}I_{3-x} network and which display an impressively enhanced stability alongside a reduced toxicity.

In the present work, we unveil the use of the large organic cation iodoethylammonium I-(CH₂)₂-NH₃⁺ (noted IEA⁺) to successfully synthesize the lead- and iodide- deficient MAPbI₃, noted d-MAPI-IEA, as thin films. They have been characterized by X-Ray Diffraction (XRD) and UV-Visible absorbance measurements. The resulting d-HP films have been additionally characterized by Scanning Electron Microscopy (SEM) and time-resolved photoluminescence (TRPL) to assess the impact of PbI⁺ units octahedra substitution by IEA⁺ on the optoelectronic and morphological properties of the perovskite layer. Finally, d-MAPI-IEA thin films have been incorporated in operational FTO/c-TiO₂/m-

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TiO₂/PVK/spiro-OMeTAD/Au PSC structure (with c-TiO₂ a compact TiO₂ layer and m-TiO₂ a mesoporous TiO₂ layer) to prove the feasibility of such photovoltaic devices and a final efficiency of 9.54 % was achieved.

2. EXPERIMENTAL SECTION

Fluorine-doped SnO₂ (FTO) substrates (TEC 7 from Pilkington) were etched pattern by zinc oxide powder and 10 % HCl solution prior to be cleaned with soap and water. The substrates were subsequently plunged for 20 min in a concentrated 2.2 M NaOH in ethanol/water (10:1 volume ratio) and cleaned in acetone using an ultrasonic bath for 12 min. They were then rinsed with deionized water in an ultrasonic bath for 15 min.²⁹ The substrates were subsequently heated at 500 °C for 15 min. The compact TiO₂ electron transporting layer (ETL), noted c-TiO₂, was prepared by aerosol spray pyrolysis as detailed in Ref. ³⁰. The anatase TiO₂ NR30-D paste (from Greatcell Solar Materials) was diluted in ethanol with a 1:7 w/w ratio. 45 μL of the solution was dropped onto the compact TiO₂ layer and spin-coated at 2000 rpm for 15 s. The layer was then dried on a hotplate at 70 °C for at least 10 min and finally heated at 500 °C under an air flux for 30 min, cooled down to 200 °C and removed from the hotplate before being transferred immediately to a N₂-filled glovebox for perovskite layer deposition.

The perovskite layers were deposited using a one-step spin-coating method. For the MAPbI₃ layer, a perovskite precursor solution with a concentration of 1.35 M was prepared by mixing 214.6 mg of MAI (Greatcell Solar Materials) and 622.3 mg of PbI₂ (TCI) in 1 mL of DMSO. The solution, placed in a tightly closed bottle, was stirred for 2 h at 100 °C in a N₂-filled glovebox. 40 μL of this solution was placed on top of the substrate before starting the spin-coating in a N₂-filled glovebox. The spinning routine used was: 1000 rpm with an acceleration of 200 rpm/s for 10 s followed by a second spinning at 6000 rpm for 30 s with an acceleration of 4000 rpm/s. 100 μL of chlorobenzene was dripped 30 s after the start of the spinning routine at a slow speed. The films were then annealed on a hotplate at 105 °C for 1h inside a N₂ filled glovebox.

For the d-MAPI-IEA, a perovskite precursor solution with a concentration of 1.0 M was prepared by mixing 132.5 mg of MAI (Greatcell Solar Materials), 384.2 mg of PbI₂ (TCI) and 176.3 mg of (IEA)₂PbI₄ (n=1 MAPbI₃-IEAI precursor) in 1 mL of DMF. The solution, placed in a tightly closed bottle, was stirred for 3 h at 50 °C in a N₂-filled glovebox. 40 μL of this solution was placed on the top of the substrate before starting the spin-coating in a N₂-filled glovebox. The spinning routine used was: 1000 rpm with an acceleration of 500 rpm/s for 10 s followed by a second spinning at 5000 rpm for 30 s with an acceleration of 1500 rpm/s. 100 μL of chlorobenzene was dripped 15 s after the start of the spinning routine at slow speed. The films were finally annealed at 150 °C for 1 hour. To finish the cells, a Spiro-OMeTAD layer was spin-coated and a gold back contact electrode was thermally evaporated as described in Ref. ³⁰.

Perovskite film structure was characterized using a PANalytical X-Pert high-resolution XRD operated at 40 kV and 45 mA and using the Cu K α radiation with $\lambda = 1.5406 \text{ \AA}$. The film specular absorbance was measured by a Cary 5000 UV-vis-NIR spectrophotometer using an integrating sphere. A glass/FTO/c-TiO₂/m-TiO₂ sample was used for the baseline. The time-resolved photoluminescence (TRPL) measurements were performed under a microscope lens (numerical aperture 0.7). The perovskites layers were spin-coated onto a glass/FTO/c-TiO₂/m-TiO₂ substrate. The top of the PVK layer was excited by a 470 nm diode laser (Picoquant) filtered by a 488 nm long pass filter. The emission was analyzed for TRPL decay by a PerkinElmer SPCM avalanche photodiode combined with a PicoHarp acquisition card (500 ps characteristic time of the total system response function) used with the laser in a pulsed mode at a 10 nW excitation power (pulse duration 70 ps). The solar cells *J-V* curves were recorded by a Keithley 2410 digital source meter, using a 0.1 V.s⁻¹ voltage scan rate. The solar cells were illuminated with a solar simulator (Abet Technology Sun 2000) filtered to mimic AM 1.5G conditions (100 mW cm⁻²). The illuminated surface was delimited by a black mask with an aperture diameter of 3 mm. The power density was calibrated at 100 mW cm⁻² by the use of a reference silicon solar cell.

3. RESULTS AND DISCUSSION

All the perovskite solar cells depicted here were fabricated using a direct mesoporous architecture consisting of an FTO-coated glass as substrates, a combination c-TiO₂ and m-TiO₂ layers as electron transporting layer (ETL), perovskite (PVK) as the absorber, Spiro-OMeTAD as hole transporting layer (HTL) and gold as counter-electrode (**Figure 1a**). The d-HP presently studied consists in a classic 3D MAPbI₃ in which we substituted PbI⁺ units by iodoethylammonium

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(IEA⁺) large organic cation. A schematic representation of the crystallographic structure of the classic 3D MAPbI₃ and the resulting d-MAPI-IEA is shown in **Figure 1b**. Both systems were thoroughly investigated and optimized.

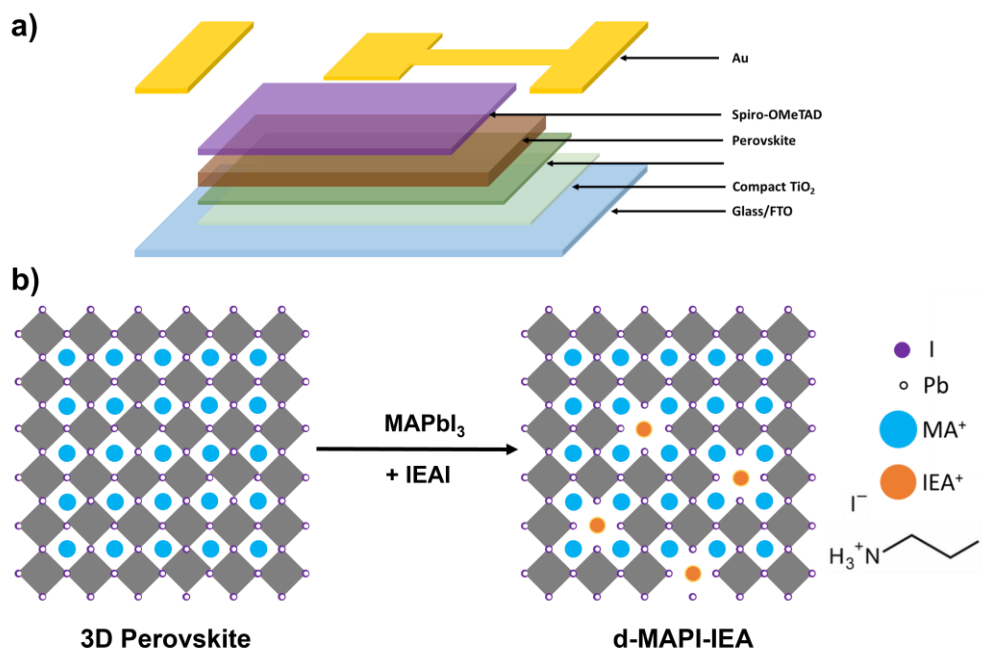


Figure 1: (a) Exploded schematic view of the perovskite solar cell structure. (b) Schematic representation of classic 3D MAPbI₃ and of 3D d-MAPI-IEA perovskite formed after partial substitution of PbI⁺ units by IEA⁺ cations.

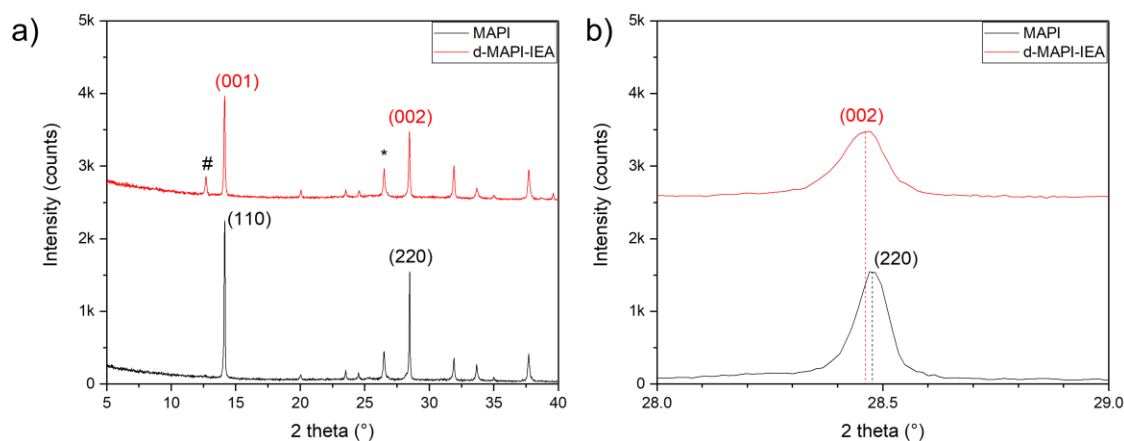


Figure 2: (a) XRD patterns of MAPbI₃ and d-MAPI-IEA perovskite films (FTO peaks are indicated by *. # symbol represents PbI₂) (b) Same as (a) zoomed between 28-29°.

X-Ray diffractions patterns depicted in **Figure 2a** show a slight reduction of the perovskite (001) and (002) peaks of the d-MAPI-IEA compared to its classic MAPbI₃ (110) and (220) analogues. Also, a non-negligible PbI₂ peak at 12.7° is present for d-MAPI-IEA. These elements suggest a lower crystallinity of the perovskite caused by the IEA⁺ cations insertion within the MAPbI₃ lattice to form the d-HP. In **Figure 2b**, a shift of the Bragg reflections to smaller 2θ angles

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for d-MAPI-IEA, indicates an expansion of the unit cell. This expansion proves the good insertion of IEA⁺ within the MAPbI₃ lattice and thus the correct formation of the d-MAPI-IEA compound as described and proved for other few systems in the past by our groups^{27,28}.

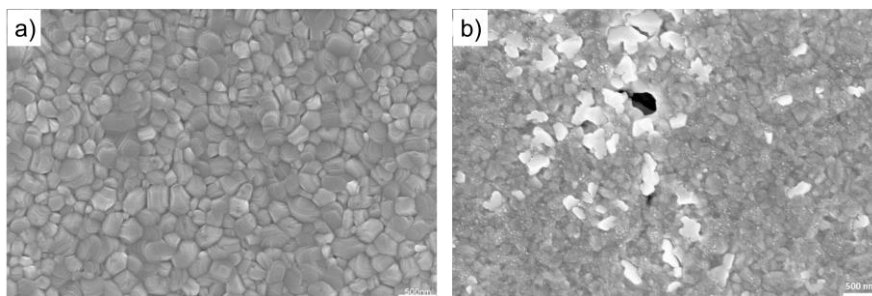


Figure 3: Top-view SEM of (a) MAPbI₃ and (b) d-MAPI-IEA perovskite films. Scale bar: 500 nm.

Top-view SEM images were obtained to assess the morphology of the d-MAPI-IEA film. The film presents important pinholes (**Figure 3b**) and PbI₂ flakes (white flakes) which are not observed for the MAPbI₃ film (**Figure 3a**). Furthermore, the d-MAPI-IEA film is constituted of rather small grains. These facts agree with the reduced crystallinity and the PbI₂ peak observed previously on the XRD patterns (**Figure 2**). The presence of IEA⁺ thus causes a consequent downgrading of the perovskite morphology that will be shown to greatly hinder the devices efficiency and the potential of this d-HP for photovoltaic applications.

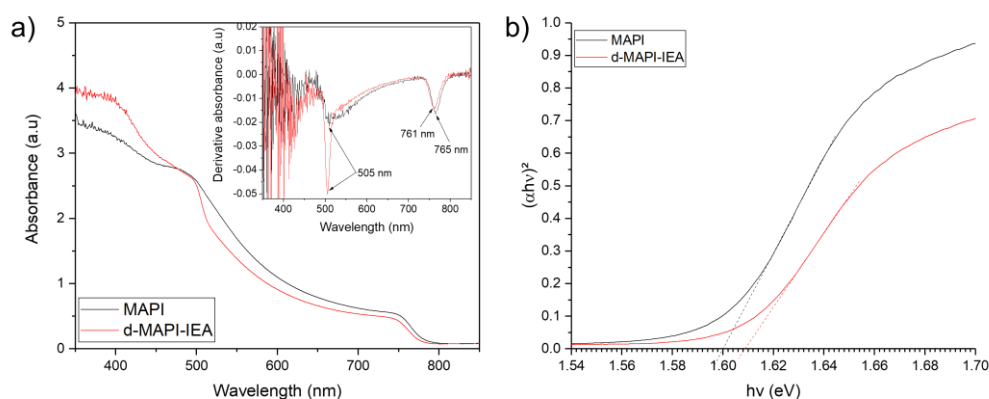


Figure 4: (a) UV-Visible spectra of MAPbI₃ and d-MAPI-IEA perovskite films. Inset: the associated derivative absorbance. (b) Tauc Plot associated to the UV-Visible absorbance spectra.

The UV-Visible absorbance spectrum of the optimized d-MAPI-IEA film was measured and compared to the reference MAPbI₃ (**Figure 4a**). The two films presented an absorbance edge in the 760-770 nm range. An additional edge at 505 nm was clearly observed after IEA⁺ insertion, causing the d-MAPI-IEA to have a better absorbance below 505 nm. For a similar d-HP, the d-MAPI-HEA, a comparable edge was found at 555 nm and was attributed to the presence of domains with a high substitution level of PbI⁺ by HEA⁺ which cause the perovskite film to become slightly reddish.^[27] In the case of d-MAPI-IEA, the same trend is observed. Indeed, as the content of IEA⁺ within the lattice increases, the perovskite layer becomes red (**Figure 5**). In our case, despite the low substitution level of PbI⁺ by IEA⁺ used, domains with important substitution rate could exist and explain the presence of the absorbance edge at 505 nm. All over the rest of the UV-Visible region, the d-MAPI-IEA displays an inferior absorbance, which counteracts the beneficial aforementioned effect. The derivative absorbance highlights a slight blue-shift of the absorption edge around 760-770 nm, caused by

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direct optical transition in the metal-organic perovskite absorber. We confirmed this blue-shift by plotting the Tauc plot of the absorbance spectra (**Figure 4b**). This allowed us to extract the optical bandgap values of MAPbI₃ and d-MAPI-IEA perovskites at 1.60 eV and 1.61 eV, respectively. Such an increase of the bandgap value was expected with the expansion of the unit cell volume caused by IEA⁺ cations insertion within the perovskite lattice and conclude the proof of formation of the d-HP d-MAPI-IEA.

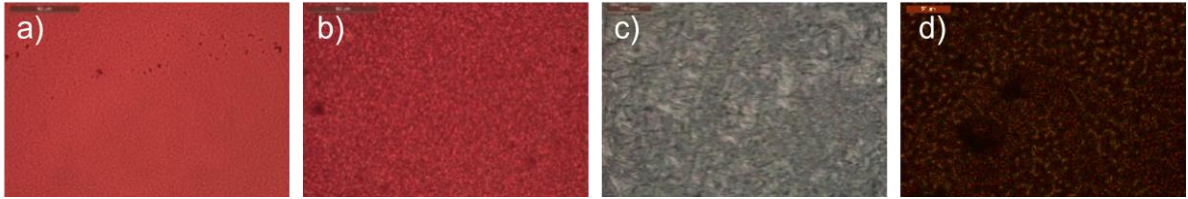


Figure 5: Optical microscope pictures of d-MAPI-IEA films for Pb/MA/IEA molar ratios of (a) 1/0.5/1 (b) 1/0.66/0.66 (c) 1/0.75/0.5 and (d) 1/0.8/0.4 (IEA⁺ content decreases from a) to d))

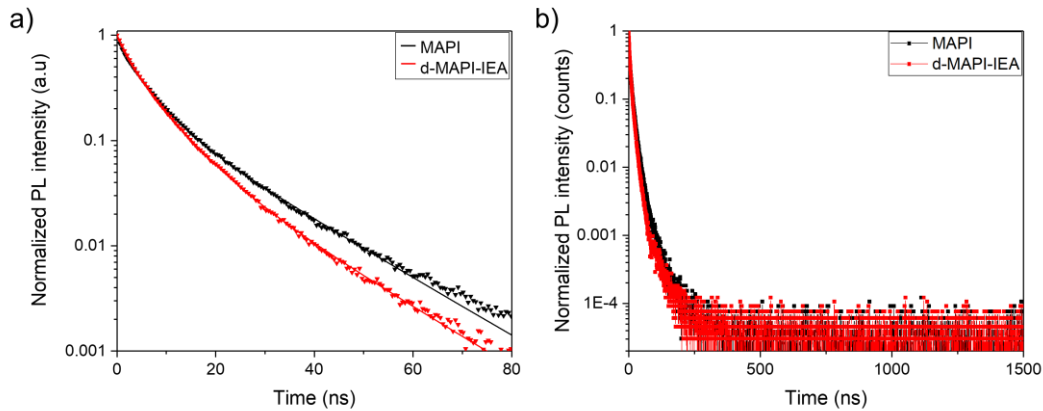


Figure 6: Normalized time-resolved photoluminescence of MAPbI₃ and d-MAPI-IEA films on FTO/c-TiO₂/m-TiO₂ substrates. (a) Zoom between 0-80 ns. (b) Measurement over 1500 ns. The full lines are the fitting curves obtained from the triple exponential fitting of the experimental points (downward triangles).

Table 1: Exponential function for TRPL fitting and extracted parameters

ExpDec3 : $y = y_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$							
Sample	y_0	A_1	τ_{fast}	A_2	τ_{int}	A_3	τ_{slow}
MAPbI ₃	4.14E-5	0.19	0.72	0.58	5.00	0.23	15.62
d-MAPI-IEA	3.49E-5	0.57	6.20	0.30	2.20	0.13	15.14

We also conducted TRPL measurements on the films deposited on FTO/c-TiO₂/m-TiO₂ substrates. Decay curves are presented in **Figure 6**. All the curves were fitted with a triple exponential function in order to obtain the best coefficient R² parameter. The function used and the fitting parameters extracted are gathered in **Table 1**. This allowed us to extract τ_{fast} and τ_{slow} , which represent the non-radiative recombination at the ETL/PVK interface (reflecting the speed of charge injection in the oxide transport layer) and the bimolecular recombination in the bulk of the perovskite (reflecting the bulk trap density), respectively. A higher τ_{slow} means a better bulk structural quality of the perovskite. In the meantime, a lower τ_{fast} value indicates a better charge extraction at ETL/PVK layer, therefore lower interface recombination centers

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and defect density. In one hand, d-MAPI-IEA film exhibited a higher τ_{fast} value than MAPbI₃ (6.20 ns vs 0.72 ns) which indicates a lower quality of the TiO₂/PVK interface caused by the presence of IEA⁺ cations and implies a higher recombination centres density that will limit the short-circuit current density (J_{SC}) and Fill Factor (FF) of the final PSCs. It also implies a slower electron injection that will aggravate the hysteresis (HI) phenomenon. On the other hand, d-MAPI-IEA exhibits a slightly lower τ_{slow} value than MAPbI₃ (15.14 ns versus 15.62 ns), emphasizing a slight downgrading of the structural quality of the perovskite caused by IEA⁺ insertion into the lattice. This less quality bulk perovskite is consistent with the morphology observed by SEM and the diffractograms obtained by XRD previously.

Once d-MAPI-IEA was proved to be a d-HP and fully characterized as thin films, we explored its potential for an application in PSCs by conducting J - V measurements. d-MAPI-IEA devices reached a maximum power conversion efficiency (PCE) of 9.54 % on reverse scan, with $V_{OC} = 1.01$ V, $J_{SC} = 17.21$ mA/cm², $FF = 54.80$ % and $HI = 51.0$ % ($PCE = 4.67$ % in forward scan). As a comparison, its analogue classic MAPbI₃ delivered a maximum efficiency of 18.94 %, with $V_{OC} = 1.04$ V, $J_{SC} = 22.29$ mA/cm², $FF = 81.44$ % and a hysteresis of 14.5 % ($PCE = 16.20$ % in forward scan) (**Table 2**). Associated J - V curves are shown in **Figure 7a**. Box charts of statistical J - V parameters values of MAPbI₃ and d-MAPI-IEA are displayed in **Figure 7b-f**. Such efficiencies were expected and can be explained by the less ETL/PVK interface quality as well as less XRD characteristics and morphology. The system also suffers from an important hysteresis. However, this issue is shared by all the d-HPs studied. Despite low PCE values, the feasibility of d-MAPI-IEA-based PSCs has been proved.

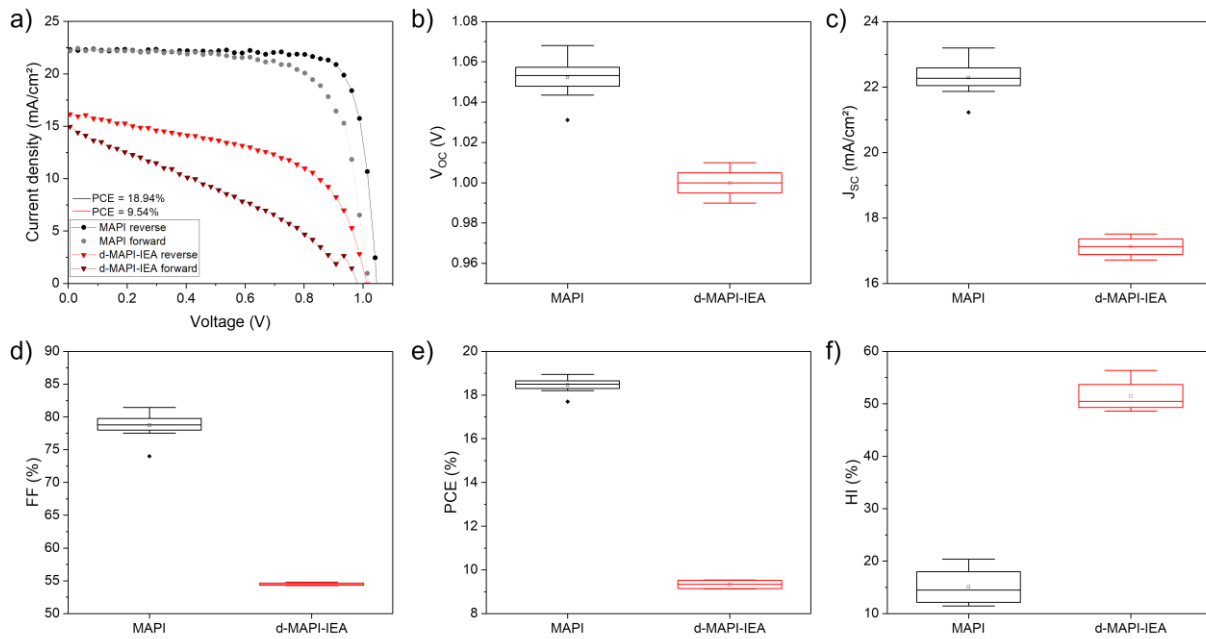


Figure 7: (a) J - V curves of best MAPbI₃ and d-MAPI-IEA devices with measured reverse scan PCEs. (b-f) Box charts of MAPbI₃ and d-MAPI-IEA PSCs J - V parameters, PCE and HI .

Table 2: Best MAPbI₃ and d-MAPI-IEA cells J - V curve parameters, PCE , and HI .

Cell	Scan direction	V_{OC} (V)	J_{SC} (mA.cm ⁻²)	FF (%)	PCE (%)	HI (%)
MAPbI ₃	Reverse	1.04	22.29	81.44	18.94	14.5
	Forward	1.02	22.33	71.29	16.20	

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d-MAPI-IEA	Reverse	1.01	17.21	54.80	9.54	51.0
	Forward	0.98	15.11	31.67	4.67	

4. CONCLUSION

In the present paper, we report the successful synthesis of a new d-HP based on the use of the iodoethylammonium (IEA⁺) organic cation. Lead -and iodide- deficient d-MAPI-IEA has been fabricated. The use of this perovskite in PSCs has been proven feasible. However, after diverse characterizations, d-MAPI-IEA has been found to display a downgraded structural quality along with a lower quality of the oxide ETL/PVK interface which limit its potential. Nevertheless, we believe that the replacement of the TiO₂ oxide layers on which was deposited d-MAPI-IEA by other oxide ETL such as SnO₂ or ZnO maybe be useful and revive the interest of this perovskite.

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