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Enhancing stability of hybrid perovskite solar cells by imidazolium incorporation

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Andrei Gabriel TOMULESCU¹, Lucia Nicoleta LEONAT¹, Florentina NEAŢU¹, Viorica STANCU¹, Vasilica TOMA¹, Sarah DERBALI², Ștefan NEAŢU¹, Arpad Mihai ROSTAS¹, Ioana PINTILIE¹, Mihaela FLOREA¹

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¹ National Institute of Materials Physics, Atomistilor 405A, 077125 Magurele, Ilfov Romania

⁹ ²Laboratory of Condensed Matter physics, Department of Physics, Ibn Tofail University, 14000 Kenitra,
 Morocco

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12 E-mail: mihaela.florea@infim.ro

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Abstract: Hybrid perovskites based solar cells have demonstrated high conversion 14 efficiency but poor long-term stability. This study reports on the results obtained after doping 15 the CH₃NH₃PbI_{2.6}Cl_{0.4} mixt halide perovskite with imidazolium (C₃N₂H₅⁺, denoted IM) on the 16 17 "A site" position of a perovskite to improve photovoltaic performances and stability of hybrid perovskite solar cells. The perovskite films were investigated by morphostructural 18 characterization techniques: X-ray diffraction, Atomic Force Microscopy, scanning electron 19 20 microscopy, UV-Vis, X-ray photoelectron and Electron Paramagnetic Resonance spectroscopies. The photovoltaic parameters were determined by measuring the IV curves of 21 22 the corresponding solar cells. The amount of IM inserted in the perovskite play a key role and therefore for a certain composition, the IM substituted perovskite film possesses an improved 23 film quality and crystallinity as compared to the pristine film. Substitution of MA⁺ with IM⁺ 24 provides a favorable way to reduce recombination processes, and also has shown great potential 25 26 to achieve high stability and enhances the power conversion efficiency of the solar cells. The optimal percentage of doping with imidazole to obtain better stability of solar cells is 6%. We 27 also calculated new tolerance factors according to the "globularity factor" and thus demonstrate 28 that at doping concentrations greater than 20% for CH₃NH₃PbI_{2.6}Cl_{0.4} perovskite the 3D 29 30 structure is no longer obtained.

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- 34 photovoltaics
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1. Introduction

With the discovery that hybrid perovskites possess exquisite semiconductor properties, a 37 new horizon has opened up in the research of thin-film solar cells: perovskite based solar cells 38 (PSCs). Briefly, the photo-physical properties that made these materials famous are: an 39 optimum direct band gap of ~ 1.5 eV, which allows an optimum collection of the high energy 40 section of the visible solar spectrum [1][2][3][4], a high absorption coefficient > $1.5 \cdot 10^4$ cm⁻¹ 41 [5], coupled with a small exciton binding energy that allows an easy separation of charges at 42 low temperatures (~50 meV) [6], a high carrier mobility (12.5 cm²/Vs for electron and 7.5 43 cm²/Vs for holes) [7] and a long carrier diffusion length (100-1000 nm) [8],[9]. Just as 44 45 important is their fabrication procedure, which is quite simple and adaptable compared to many 46 other materials for photovoltaic applications. Thus, scientific literature presents many techniques appropriate to engineer thin layers of hybrid perovskite materials, more commonly 47 used are: spin coating [10],[11], dip coating [12], thermal evaporation [13], and screen printing 48 [14]. Albeit their efficiency record surpassing 24% for small active area devices [15], 49 50 considerable effort is still invested to fix the stability issues. Many reports revealed that with a 51 proper composition tuning of the hybrid perovskite, via substitution or by doping either the A-52 site, B-site or X-site ions, can improve the stability and the device performances [16],[17].

The design and development of new hybrid perovskites for various photovoltaic (PV) 53 applications must be tailored in correlation with their electronic properties, structure and 54 55 composition. Nevertheless, irrespective of the targeted PV application, an extremely important feature is the fabrication of a compact perovskite film with a high degree of surface coverage, 56 57 crystallinity and homogeneity, which is the key for a good device. If the perovskite film contains defects, such as pinholes, rapid degradation is enabled by allowing moisture 58 penetration, facilitating local changes in composition and structure, subsequently resulting the 59 rapid degradation of the entire device [18], [19]. Consequently, many approaches have been 60 employed to improve the quality of the perovskite films, from mixing different organic/ 61 inorganic cations [20], [21] to "polyelemental multicomponent engineering" [22], while the 62 ABX₃ structure and therefore the Goldschmidt tolerance factor [23] remain unaffected. 63

Metyhlammonium lead iodide (MAPbI₃, MAPI) is the most widely used perovskite as light absorber and devices using this specific composition achieved maximum PCEs of 15% [24]. However, MAPbI₃ is unstable when exposed to light, heat, moisture and oxygen [25] and thus different strategies were adopted in order to encompass these drawbacks. For example, the incorporation of 5-aminovaleric acid (5-AVA) in MAPbI₃ enables a PCE of 12.8% and shows

better stability under illumination compared to pure MAPbI₃ [26]. Furthermore, in the case of 69 the organic cation, the rule "the more the better" seems to be applied since devices with 70 formamidinium (FA) and cesium (Cs) mixed with methylammonium (MA) have delivered an 71 impressive PCE >20% and ~18% after 250 hours under operational conditions [27]. In fact, the 72 73 main culprit for the instability of the photoactive layer was identified in the organic cation 74 component [28] due to its volatility. One approach to stabilize the perovskite structure is to use 75 larger cations such the ones from the ionic liquids [29]. Larger cations are used as additive in 76 the perovskite precursor solution and as interface modifiers at both perovskite interfaces with the charge selective layers [30], [31], due to their versatility in molecular structure, increased 77 78 ionic conductivity and mechanical stability.

Imidazolium iodide (IMI) is an ionic salt composed of an organic cation, imidazolium 79 (chemical formula $C_3N_2H_5^+$, shortly IM⁺), and an inorganic anion, iodide (I⁻), characterized by 80 its weak interaction, which translates into a reduced tendency to crystalize caused by the 81 imbalance induced by the large cation and the small and delocalized anion. In dye sensitized 82 solar cells with solid electrolyte, IMI was used to increase the conductivity of the electrolyte, 83 to improve the charge transfer inside the electrolyte as well as at the interfaces and to enhance 84 long-term stability by preventing dye aggregation and regenerating the oxidized dyes [32], [33]. 85 86 Other groups also report that imidazolium improves the PCE for dye-sensitized solar cells DSSCs [34], [35], either by passivating the volume defects acting as a Lewis base, neutralizing 87 88 the excess of positive charge of the Pb atoms within the crystal forming a coordinate covalent bond [36], [37], or by passivating the surface, as reported recently in the work of Salado et al., 89 90 by the adjustment of the surface texture, electrical properties, and crystallization of the perovskite films [38]. Goldschmidt tolerance factor (t) calculations support the formation of 91 92 imidazolium perovskites, as shown for IMPbX₃ ($X = Cl^{-}$ and I^{-}) compounds with tolerance 93 factor values of 1.03 for (IMPbCl₃) and 0.99 for (IMPbI₃) which coincide with the accepted t94 values reported for the ideal perovskite structure (0.8 < t < 1) [39].

- In this study, we investigate the effect of gradual replacement of MA⁺ with IM⁺ upon structural, optical and electronic properties as well stability of the perovskite films. These layers were used as photoactive parts to fabricate solar cells in a mesoscopic geometry, with the compact and mesoporous TiO₂ as n-type semiconductor. Different compositions of organic-inorganic perovskites based on methylammonium and imidazolium solutions (MA_xIM_{1-x}PbI_{2.6}Cl_{0.4}, with x = 0 to 1) were synthesized and thoroughly characterized. However, our study focused on complex perovskites with lower quantities of IM doping, where x < 0.2.
- 102 The photovoltaic performance of the studied films was probed by fabricating mesoscopic

103 n-i-p devices with FTO/ TiO₂compact/ TiO₂mesoporous/ $MA_{1-x}IM_xPbI_{2.6}Cl_{0.4}$ / Spiro-104 OMeTAD/ Au configuration. The schematic architecture of the perovskite solar cells (PSCs) 105 used in this study is shown in Figure S1.

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107 **2. Experimental**

108 All the precursors and solvents were purchased as follows: lead iodide (PbI₂, Sigma Aldrich 99%), lead chloride (PbCl₂, Sigma Aldrich 99.99%), methylammonium iodide (MAI, Dyesol), 109 imidazole (Sigma Aldrich 99%), dimethyl sulfoxide (DMSO, Alfa Aesar 99%), N,N-110 dimethylformamide (DMF, Alfa Aesar 99.8%), titanium diisopropoxide bis(acetylacetonate) 111 (Ti(iProp)₂AcAc₂, Sigma-Aldrich, 75 wt. % in isopropanol), TiO₂ commercial paste (Solaronix 112 Ti-Nanoxide N/SP), hydroiodic acid (Alfa Aesar 47 wt. % in water) isopropanol (IPA, Sigma 113 Aldrich, anhydrous), absolute ethanol (Alfa Aesar, anhydrous), diethyl ether (DEE, Alfa Aesar, 114 99%). All salts and solvents were used as received without any further purification. 115

116 2.1. Preparation of the imidazolium iodide and perovskite solution

For the preparation of imidazolium iodide $(C_3N_2H_5I)$ the following procedure was employed: inside a 50 mL round bottom flask with three opening, an imidazole solution (40 wt. % in absolute ethanol) was mixed with 5 mL hydroiodic acid (47 wt. % in water) by stirring at 0 °C, under N₂ atmosphere, in a molar ratio of imidazole $(C_3N_2H_4)$ to hydroiodic acid of 1:1. Crystallization of $C_3N_2H_5I$ was achieved by keeping the round flask containing imidazole and hydroiodic acid at room temperature under N₂. The yellowish-white precipitate was washed several times with diethyl ether and then dried at 60 °C overnight under vacuum.

Perovskite precursor solutions were prepared to obtain MA_{1-x}IM_xPbI_{2.6}Cl_{0.4} (respectively 124 125 $[CH_{3}NH_{3}]_{1-x}[C_{3}N_{2}H_{5}]_{x}PbI_{2.6}Cl_{0.4}$ solutions where x = 0, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, 0.10, 0.20, 0.25, 0.50, 0.75, 1.00 resulting a total molar concentration of 1.415 in a mixture of DMF 126 127 and DMSO (molar ratio 8.2:1). All solutions were magnetically stirred for at least 1h at room temperature. The samples were named according to the IM content, for example IM6 is a sample 128 with x = 0.06, meaning a perovskite composition of MA_{0.94}IM_{0.06}PbI_{2.6}Cl_{0.4}. For x = 0, we 129 named the perovskite MAPI and for x = 1, the organic cation is fully replaced with IM and 130 became IMPI. 131

132 2.2. Device fabrication

Substrates: FTO coated glass slides (10 ohm/sq from Xin Yan Technology LTD) were
 washed with a detergent solution, and rinsed with plenty of distilled water, followed by

sonication in acetone and then in ethanol in an ultrasonic bath for 10 min for each solvent.Finally, an oxygen plasma treatment was applied for 15 min at 0.7 mbar.

137 *Compact TiO*₂ (*TiO*₂*c*). Using an in house automated setup, the layer was fabricated by 138 spray pyrolysis using an isopropyl alcohol solution of Ti(iProp)₂AcAc₂ (1:30 weight ratio), 139 using 30 spray sweeps keeping the nozzle at 15 cm height and 450 °C substrate temperature, 140 with N₂ as a carrier gas at 2 kgf/cm² pressure and a sweep speed of 50000 μ m/s. After the 141 deposition, the samples were treated at 450 °C for 30 min on the hot plate.

Mesoporous TiO_2 (TiO_2m). Using the same setup, a dispersion of TiO_2 nanoparticles in 142 ethanol (1:100 weight ratio) was deposited using 30 spray sweeps, at 15 cm height, 100 °C 143 substrate temperature, using N₂ at 2 kgf/cm² pressure and at a sweep speed of 50k μ m/s. A 144 145 solvent drying treatment at 100 °C for 5 min on the hot plate was used after the deposition. Then the TiO₂m films were thermally treated at 500 °C for 1 h, with a heating ramp of 5 °/min. 146 147 Hybrid perovskite of different composition [CH₃NH₃]_{1-x}[C₃N₂H₅]_xPbI_{2.6}Cl_{0.4}, was fabricated by spin-coating, inside an in-house glove box that was continually purged with N₂, at room 148 149 temperature (25 - 26 °C) and humidity below 10% using the above-described solutions at 2000 rpm for 25s. At 12 s from the start of the process 100 µL of the antisolvent DEE was dropped 150 151 dynamically onto the sample. A thermal treatment at 100 °C for 3 min was applied to obtain the crystalline perovskite film. 152

Spiro-OMeTAD was used as hole transport material (HTM), and fabricated it as a thin film 153 by spin-coating a mixture of 80 mg spiro-OMeTAD (Borun Chemical), 28 µL 4-tert-154 butylpyridine (Sigma Aldrich, 96%) and 18 µL of bis(trifluoromethane) sulfonimide lithium 155 salt (Alfa Aesar, 98%) in acetonitrile (Sigma Aldrich, 99.8%, anhydrous) solution (520 156 mg/mL), all dissolved in 1 mL of chlorobenzene (Sigma Aldrich, 99.8% anhydrous). This 157 solution was spun at 3000 rpm for 30 s, inside glove box with low humidity (below 10%), at 158 159 room temperature. The samples were left in low humidity environment, < 10%, overnight to dry and oxidize the HTM. 160

The devices were completed by sputtering Au electrodes of approx. 70 nm thickness
through shadow masks defining squares of 0.09 cm² active area.

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164 2.4. Characterization

165 <u>Device measurement protocol</u>. Current-voltage characteristics were measured under 166 simulated sunlight AM 1.5G, 100 mW/cm² from an Oriel VeraSol-2 Class AAA LED Solar 167 Simulator, coupled with a Keithley 2400 source meter. The solar simulator was calibrated with an NREL certified KG5 filtered Si reference diode to an irradiation intensity of 100 mW/cm². The devices were masked to make sure that only the active area was illuminated during measurement. Electrical measurements were performed in ambient environment, around 25 °C, starting just above the V_{oc} to J_{sc} and backward, at 20 mV/s, to avoid the sample pre-poling. All devices were measured in air without encapsulation.

<u>DR-UV-Vis spectroscopy</u> (AvaLight-Xe pulsed light source connected to an AvaSpec-ULS
 2048L spectrometer equipped with an AvaSphere 80-REFL integration sphere) was used to
 investigate the optical properties of the solid samples. The spectra were recorded in the range
 of 200–800 nm by using BaSO₄ as baseline.

177 <u>X-ray Diffraction (XRD)</u> spectra were recorded in symmetrical coplanar geometry, using a 178 Bruker AXS (D8 ADVANCE), with a Cu anode as the source and a Ni filter to eliminate the 179 Cu-K β contribution to the detected signal, with a dichromatic (Cu-K $_{\alpha 1}$ = 1.54060 Å and Cu-K $_{\alpha 2}$ 180 = 1.544 Å) incident beam. The maximum intensity peaks of the perovskite layers were further 181 analyzed by fitting with the Gaussian distribution in order to exactly determine its position and 182 the value of the full width at the half maximum (FWHM). The crystallite size was calculated 183 using the Scherrer equation.

<u>Scanning Electron Microscopy (SEM)</u> images were recorded using a Carl Zeiss Gemini 500
 Field Emission Scanning Electron Microscope. The samples were imaged using an acceleration
 voltage of 5 kV (EHT), a working distance between 3 and 8 mm (WD) and different
 magnifications in high vacuum mode. Optical microscopy images were obtained using a Zeiss
 Axio Scope.A1 in reflection mode at 20x magnification.

<u>Atomic Force Microscopy (AFM)</u> images and roughness measurements were determined
 using an atomic force microscope NT-MDT Aura Ntegra Prima in noncontact mode.

X-ray Photoelectron Spectroscopy (XPS) analyses were done operating an Al-Ka 191 monochromated radiation (hv = 1486.74 eV, X-ray source) on a Kratos Ultra DLD Setup 192 193 apparatus (Kratos Analytical Ltd., Manchester, UK). The spectrometer was calibrated at 84.0 eV (Au 4f_{7/2}). All XP spectra were registered in the following conditions: pressure 1×10^{-7} Pa, 194 power of 225 W (15 kV × 15 mA) and charge neutraliser. The fittings were realized using Voigt 195 profile. Samples containing Au electrode were calibrated using at 84.0 eV, while for the 196 samples missing gold C 1s line (BE = 284.6 eV, C–C (CH)_n bonds) was used as standard to 197 calibrate the measured devices. 198

Electron Paramagnetic Resonance (EPR) measurements were carried out with a continuous 199 wave X-Band EPR Bruker EMX plus spectrometer equipped with a Bruker ER 4104OR Optical 200 Transmission X-band resonator coupled with a light source calibrated with NREL certified KG5 201 filtered silicon reference diode. The measurement parameters for the X-Band measurements if 202 not otherwise mentioned were set as follows: microwave frequency 9.4621 GHz, microwave 203 power 2 mW, modulation amplitude 0.4 mT, receiver gain 2×10^3 , conversion time 83 ms, time 204 constant 40.96 ms, number of points 6000 and number of scans 2. The time sweep experiments 205 were carried out with the following parameters: microwave frequency 9.4621 GHz, microwave 206 power 2 mW, modulation amplitude 0.2 mT, receiver gain 2×10^3 , conversion time 400 ms, 207 time constant 163 ms, sweep time 3600 s and number of points 9000. The measured light 208 209 intensity at the working distance corresponds to 0.5 sun. All EPR measurements were carried 210 out at room temperature.

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3. Results and discussion

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Imidazolium has a large size ionic radius ($r_{IM} = 258 \text{ pm}$) compared to the one of MA (r_{MA}) 213 = 217 pm) but quite close to the one of formamidinium (FA) of r_{FA} = 253 pm, which translates 214 into perovskite 3D structures with t = 0.9147 for MAPbI_{2.6}Cl_{0.4} and t = 1.0016 for IMPbI_{2.6}Cl_{0.4}. 215 However, a new study reveals that the actual values for the tolerance factor t for more complex 216 molecules like MA, FA, IM are larger than previously thought, if factors like rigidity and 217 molecular asymmetry are considered [42]. This means that the tolerance factor t for IMPI is 218 larger than previously calculated, from 1.0016 to a "corrected" value of 1.1159, revealing that 219 for IMPI, t falls out of the 0.8<t<1 regime for 3D perovskite structure formation. This is why, 220 for perovskites with larger organic cations such as IMPI, the favorable black phase does not 221 222 form even at high thermal treatments.

According to these findings, we calculated the tolerance factor for our samples and 223 presented the values in Table S1. We observed that *t* reaches 1 at x = 0.2 revealing that a stable 224 225 3D single phase structure can no longer be obtained after this concentration. For instance, at concentrations exceeding 0.2 of IM, the lattice is very stressed and breaks, forming other 226 competing perovskite phases. 227

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3.1. Characterization of the perovskite films

In agreement with this statement, for complex perovskites $MA_{1-x}IM_xPbI_{2.6}Cl_{0.4}$ with x > 230

- 0.25 the quality of the perovskite film degrades, forming a discontinuous film, as shown by the *SEM images* in Figure 1 due to the formation of different perovskite crystalline phases of MAPI
 and IMPI. SEM images show that at 10% IM concentration the perovskite film starts to lose its
 compactness exposing a large quantity of voids and pinholes. Over 50%, the films begin to
 transform into an almost dendritic network, with dense and compact bulky isolated domains.
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Figure 1. SEM images depicting the surface coverage of the IM substituted perovskite films.

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The UV-Vis absorption spectra corresponding to pristine and IM substituted perovskite films are depicted in Figure 2. From these curves, we calculated the corresponding bandgap (Eg) and the values are presented in Table 1. At low concentrations a slight decrease of the calculated Eg is observed, from 1.6382 eV for unsubstituted perovskite, to 1.6313 eV for x=0.25. This shift to lower bandgap values demonstrates that the larger IM cation is gradually inserted into the perovskite structure.

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Table 1. Eg calculated values for low concentrations of IM⁺.

| X | Eg (eV) | ±error (eV) |
|------|---------|-------------|
| 0 | 1.63823 | 0.00069 |
| 0.05 | 1.63268 | 0.00047 |

| 0.10 | 1.63266 | 0.00053 |
|------|---------|---------|
| 0.25 | 1.63131 | 0.00089 |

The addition of IM^+ influences drastically the absorption profile only at higher concentrations, exceeding 25%. When IM > 50%, the absorption profiles change considerably and the bandgap cannot be calculated anymore due to the loss of the film compactness and the formation of large bandgap non-3D perovskite structures. This happens because the larger IM cation is no longer inserted into the MAPI crystalline lattice, but forms a completely different compound, most likely the IMPI perovskite with a larger bandgap.



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Figure 2. UV-Vis absorption spectra of the pristine and IM substituted perovskite films.

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These results confirm the theoretical calculations of the tolerance factor according to the new findings (presented in Table S1) and confirm that adding IM can indeed modify the crystalline perovskite MAPI lattice but only at concentrations less than 20%. For this reason, and because the aim of this study was to fabricate solar cells where a continuous perovskite film is mandatory, we focused the study on complex perovskites $MA_xIM_{1-x}PbI_{2.6}Cl_{0.4}$, with lower quantities of IM, where x < 0.2.

X-ray diffraction analysis, presented in Figure 3 revealed the formation of a hybrid halide lead perovskite as a primary crystalline phase with tetragonal symmetry, with diffraction lines at 14.1° (110), 20° (200), 24.5° (202), 28.4° (220) and 31.8° (310) corresponding to MAPbI₃ (ICDD:01-083-7582) and at 15.6° (100) corresponding to MAPbCl₃ [43]. Lead iodide was also detected in several samples with high concentration of IM, most likely because of the environmental humidity during deposition. The main (110) MAPI peak was considered to study

- the effect of imidazolium addition on the crystal structure, using the Debye-Scherrer equation
- and all data collected are available in Table 2.
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Table 2. Average crystallite size calculated from the (110) peak.

| IM quantity | 20 MAPI (001) peak | FWHM | Crystallite |
|-------------|--------------------|-------|-------------|
| | (°) | (°) | size (nm) |
| 0 | 14.167 | 0.162 | 70 |
| 0.02 | 14.128 | 0.185 | 60 |
| 0.04 | 14.118 | 0.167 | 67 |
| 0.05 | 14.112 | 0.175 | 63 |
| 0.06 | 14.108 | 0.176 | 63 |
| 0.07 | 14.102 | 0.174 | 63 |
| 0.08 | 14.099 | 0.160 | 69 |
| 0.10 | 14.099 | 0.174 | 63 |
| 0.20 | 14.101 | 0.185 | 60 |

A small shift from 14.17° for 0% IM to 14.1° for 8% IM is observed (Figure 3 and Table 275 2), indicating the partial substitution of the MA⁺ with IM⁺ in the crystalline lattice causing a 276 277 slight increase in the unit cell volume [29]. For 10% and 20% IM perovskite films, the shift does not progress, indicating the start of the formation of IMPbI₃ perovskite phase, which is 278 279 confirmed by the presence of an additional diffraction line at 11.5° in the case of 20% IM 280 concentration. This line attributed to the formation of IMPbI₃ perovskite was also reported by other groups [44], [40]. FWHM values were also determined, resulting a variation between 281 0.185 and 0.162 corresponding to crystallite sizes of 60-70 nm, with smaller crystallite sizes 282 when MAPI was partially substituted with IM⁺. This result also suggests that the partially 283 substituted IM devices present a lower crystallinity then the pristine MAPI, probably due to the 284 285 expansion of the of the cubo-octhaedral volume of the unit cell when a larger cation enter into the structure [40]. These results are also in agreement with the AFM images of the perovskite 286 layers with different quantities of IM (0, 5, 6, 7, 10 and 20%) presented in Figure 4. 287



* - MAPbl, ^ - MAPbCl, x - IMPbl, + - Pbl, o - FTO

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Figure 3. XRD data for the pristine and IM substituted perovskite films.

All AFM images reveal continuous layers completely covering the surface. Up to 7% IM, 291 292 the films presents a uniform compact structure with typical grains of different sizes and well delimited crystalline domains. Measuring the grain size, we observe that both the average size 293 and the size values interval decrease with the increase of IM concentration as presented in Table 294 3. After that, a change in the structure occurs, and the morphology of the surface is completely 295 different. Most likely, the IMPbI₃ perovskite already starts to form at these concentrations 296 297 located at the grain boundary of the normal film in the shape of a spherical or needle like 298 formations up to 1 µm in size. As already pointed out, this is consistent with the XRD results, indicating that when the IM⁺ ion cannot be integrated for higher x values in the main perovskite 299 300 phase it segregates at the grain boundary forming the IM perovskite.





Figure 4. AFM images for the pristine and 5%, 6%, and 7% IM doped perovskite films.

Larger quantities of IM leads to an increased occurrence of pinholes as can be observed in Figure 4 in the case of 10% and 20%. Average roughness decreases because of the change in structure, from cauliflower-type crystalline bouquets to undefined surfaces with acicular formations oriented perpendicular to the surface, with roughness ranging from 94 nm (average value for 5, 6 and 7%) to 61 nm (average for 10 and 15%). This variation of the RMS value is caused by the flattening of the grain boundaries.

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| Table 3. Grain value | es of the p | erovskite films. |
|----------------------|-------------|------------------|
|----------------------|-------------|------------------|

| X (IM) | Average grain size (µm) | Grain size interval (µm) |
|--------|-------------------------|--------------------------|
| 0 | 7.8 | 3.4 - 15.5 |
| 0.05 | 3.6 | 2.1 - 4.8 |
| 0.06 | 2.8 | 1.9 - 4.0 |
| 0.07 | 2.5 | 1.2 - 3.6 |
| 0.10 | not measurable | not measurable |
| 0.20 | not measurable | not measurable |

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The surface aspect of samples with imidazolium are presented in Figure 5 through SEM images, which are in good agreement with the AFM study, where the addition of small quantities of IM (5 and 6%) facilitates the formation of a compact, thicker layer. With the increase of IM concentration pin holes start to appear, visible even at 7%. The decrease of grain
size with the increase of IM concentration is also confirmed, a greater number of grain
boundaries being visible for 7% compared with the other films.

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Figure 5. SEM images of the perovskite surface with low IM concentration: a) MAPI, b) IM5, c) IM6
and d) IM7.

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X-ray photoelectron spectroscopy (XPS) was used to evaluate the iodine migration process 322 323 and stability of the solar cells when perovskite is doped with IM⁺. For this purpose, we analysed 324 a selection of solar cells: pristine, IM6 and IM20 films. Two points on each surface of devices 325 where chosen (see Figure 7d): one directly onto the Au electrode (P3) and a second one in the 326 middle of the cell, between the electrodes (P5) to study the effect of field induced ion migration, and thus to evaluate the integrity of the perovskite composition. Moreover, the optimum doped 327 328 perovskite solar cell (IM6) was analysed in several points, to understand and evaluate the stability over time of this composition. A picture revealing was inserted in Figure 7 for clarity. 329 330 We should mention that P2 was identical with P3 in terms of results; therefore, the experimental 331 values are not represented, but confirm the XPS composition found in P3 point.

In Figure 7 a comparison of the core levels I 3d, Pb 4f and Au 4f of the three composition 0%, 6% and 20% IM doped perovskite is presented, each in two points: P3 and P5. As can be observed, at point P5, outside the Au electrode, the perovskite formulation could not be

identified since iodine is not present on the analysed surface, and only a scarce amount of Pb, 335 probably due to the slow migration of Pb to the surface. Unlike the point P5, sensitive 336 differences can be observed when the samples where measured onto the gold electrode (P3). 337 The presence of iodine was observed in considerable amount for all samples, while the other 338 elements of perovskite were not identified, demonstrating a migration of iodine through the 339 gold electrode. The iodine migration is a well-known phenomenon when Au or Ag are used as 340 electrodes [Iodine Migration and Degradation of Perovskite Solar Cells Enhanced by Metallic 341 Electrodes, doi.org/10.1021/acs.jpclett.6b02375]. However, in our case, doping the perovskite 342 with IM⁺ induce a decrease of iodine migration as discussed further. The main amount of gold 343 found at the surface of the electrode is metallic gold, as expected, while the core level I 3d 344 345 found at 619.1 eV revealed mainly the presence of I⁻ as originating from AuI [Size controllable redispersion of sintered Au nanoparticles by using iodohydrocarbon and its implications, 346 347 doi:10.1039/c5sc04283f]. As presented further, the iodine found in the perovskite has a component at higher BE (619.5 eV). 348



Figure 7. XPS spectra of I 3d (a), Pb 4f (b), Au 4f (c) for the three compositions chosen 0%, 6% and
20% IM doped perovskite and schematic representation of the points measured (d).

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Figure 8 presents the high-resolution spectra of I3d and Pb4f core levels for different stages of IM6 solar cell coverage during preparation with the last layer being: (1) the perovskite film

(IM6 without spiro), (2) Spiro-MeTAD (IM6 with spiro) and (3) gold electrode (measured in 2 354 points IM6 P3 and IM6 P5). XPS data of the cell (1) revealed the constituent elements of the 355 perovskite composition, iodine and Pb. For cell (2) and cell (3)-P5, no constituent elements 356 from the perovskite where found at the surface and no migration of iodine was identified outside 357 the gold electrode region, due most probably to Spiro-OMeTAD film which has a thickness in 358 the range of 180 - 300 nm. Iodine was detected only on the surface of the gold electrode cell 359 (3)-P3, with a lower binding energy (619.1 eV, associated with AuI) than that of iodine found 360 361 in the perovskite (619.5 eV).

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Figure 8. Comparative spectra of IMI6 solar cell with the cell at different stages: perovskite film at the
 surface (IMI6 without Spiro-OMeTAD) and Spiro-OMeTAD film at the surface (IMI6 with spiro).
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With the scope to demonstrate the stability of the devices containing perovskite substituted 367 with IM, several experiments were envisaged (see Figure 9). Thus, the core levels Au 4f and I 368 3d of IM6 were recorded in different points and in different conditions: (i) fresh, immediately 369 370 after preparation, (ii) after the first electrical measurements and (iii) after the second electrical measurement (after 40 days); the data is summarised in Figure 9 and Table 45. For all 371 experiments, irrespective of the numbers of days passed between the electrical measurements, 372 or the numbers of electrical measurements, iodine migration to the surface was observed only 373 374 on the areas where gold was present (onto the electrode (P3) or at the edge of the gold electrode (P1, P8, P9). 375





Figure 9. XPS core level Au 4f and I 3d for IM6 cells (fresh, after the first measurement and after the
second measurement).

Two components were observed for both, Au 4f and I 3d while fitting the high-resolution spectra of these chemical elements (see Table 4). The main component on the electrode surface is metallic gold, but a smaller component appears at ~84.5 eV, which was associated with $Au^{\delta+}$ that can form compounds with iodine [Size controllable redispersion of sintered Au nanoparticles by using iodohydrocarbon and its implications, doi:10.1039/c5sc04283f]. This

component is more prominent in the fresh solar cells, and almost disappears after the second 385 electrical measurements. Such behaviour can be explained by the evaporation of the iodine 386 found at the surface, phenomenon observed also by others [Reversible Formation of Gold 387 Halides in Single-Crystal Hybrid-Perovskite/Au Interface upon Biasing and Effect on 388 Electronic Carrier Injection, doi.org/10.1002/adfm.201900881]. Also, the I 3d spectra show a 389 second smaller component, which can be associated with polyiodic species I_m^{ε} (~620.1 eV) 390 [Size controllable redispersion of sintered Au nanoparticles by using iodohydrocarbon and its 391 implications, doi:10.1039/c5sc04283f], which also diminished with the electrical measurement. 392

393

Table 4. Binding energies of the component found for Au 4f and I 3d and the atomic ratio ofthe components for IM6 cell in different points and different conditions.

| Component | Au ⁰ | | $Au^{\delta +}$ | | I- | | $I_m^{\ \delta-}$ | | Atomic |
|---|-----------------|---|-----------------|--|--------|---|-------------------|--|--|
| Point | E (eV) | Atomic ratio Au ⁰ /Au _{tot} | E (eV) | Atomic ratio $Au^{\delta+}/Au_{tot}$ | E (eV) | Atomic ratio I ⁻ /I _{tot} | E (eV) | Atomic ratio $I_m^{\delta-}/I_{tot}$ | ratio I _{tot} /Au _{tot} |
| Fresh cells | • | | | | | | | | |
| P3 | 84.0 | 87 % | 84.4 | 13 % | 619.1 | 94 % | 620.0 | 6 % | 0.05 |
| P8 | 84.0 | 96 % | 84.6 | 14 % | 619.2 | 72 % | 620.1 | 28 % | 0.06 |
| P9 | 84.0 | 94 % | 84.5 | 16 % | 619.1 | 89 % | 620.1 | 11 % | 0.06 |
| After the first e | electrica | l measurem | ent | | | | | | |
| P3 | 84.0 | 95 % | 84.5 | 5 % | 619.1 | 96 % | 620.1 | 4 % | 0.05 |
| P8 | 84.0 | 96 % | 84.6 | 4 % | 619.1 | 92 % | 620.0 | 8 % | 0.05 |
| P9 | 84.0 | 96 % | 84.6 | 14 % | 619.1 | 95 % | 620.3 | 5 % | 0.08 |
| After the second electrical measurement | | | | | | | | | |
| P3 | 84.0 | 97 % | 84.6 | 3 % | 619.1 | 96 % | 620.2 | 4 % | 0.05 |
| P8 | 84.0 | 98 % | 84.6 | 2 % | 619.1 | 98 % | 620.5 | 2 % | 0.05 |
| P9 | 84.0 | 100 % | 84.6 | - | 619.1 | 95 % | 620.3 | 5 % | 0.06 |

396

Further, the Itot/Autot ratio will be discussed in detail since this can give us an idea about 397 the iodine migration process. In Table 4 can be observed that the atomic ratio I_{tot}/Au_{tot} at the 398 surface on gold electrode (P3) was found to be 0.05, slightly lower than the ratio found on the 399 400 IMO cell (0.06). However, the Itot/Autot ratio for IM6 has slightly higher values for iodine amount at the edges of gold electrode (see P9, in Table 4). Interesting to note is that for IM6, 401 contrary to the behaviour of IMO cell, the Itot/Autot ratio remains constant after the electrical 402 measurements, emphasizing that the insertion of IM⁺ cation in the classical structure of 403 perovskite lead to the improvement of the solar cell stability, migration of iodine no longer 404 taking place in time or after the electrical measurements. 405

406

To gain useful information on the effect of the IM⁺ incorporation site into the crystalline

407 structure of the perovskite we use EPR measurements on pristine and 6% doped perovskite 408 $(MA_{0.94}IM_{0.06}PbI_{2.6}Cl_{0.4})$ solar cells. Figure 10 shows the corresponding EPR signal for pristine 409 and doped solar cells before this were exposed to light.



411

410



Figure 10. EPR analysis of the pristine and IM6 perovskite (up) EPR spectra before light exposure
(bottom) time dependency of the EPR signal maximal intensity.

The EPR spectra show an isotropic strong signal at a magnetic field of 337.5 mT (pristine) and 340.6 mT (IM6). Together with the microwave frequency of 9.4621 GHz at which the measurements were carried out, the isotropic g-values can be calculated with $g_{pristine} = 2.0031$ and $g_{IM} = 1.9847$. Since it is an organic cation, we start from the assumption that the IM⁺

preferentially occupies the MA⁺ sites. Due to the different effective ionic radii of MA⁺ (2.70 419 Å) and IM⁺ (2.58Å), the replacement of MA⁺ by IM⁺ induces a local structural distortion in the 420 perovskite phase that facilitates the free radical formation. This structural modification 421 promotes the occurrence of more paramagnetic centers altering the spin lattice interaction, 422 which leads to the observed shift in the g-value for higher IM⁺ concentrations. This is in good 423 agreement with XRD data, where we observe a shift to lover angles of the [001] peak, 424 characteristic to the perovskite, Table 2. The changes in g factors, from $g_{pristine} = 2.0031$ to g_{IM} 425 = 1.9847, in the system indicate that the local magnetic field experienced by the electron is not 426 427 identical, suggesting that the structure of the material is strongly influenced by the dopant. The 428 EPR signal at around 160 mT with a g-value of 4.214 characteristic for iron impurities, 429 originates from the glass substrate on which the solar cell layers are deposited and is not influencing the EPR signal of the solar cell (data not shown). 430

431 The two solar cells were then exposed to light and the changes of the EPR signal intensity were again monitored as depicted in Figure 10. To detail the signal dependency under light 432 433 exposure the magnetic field was fixed to the value corresponding to the maximum of each EPR signal (337.2 mT (pristine) and 340.3 mT (IM6)) and the signal intensity was measured as a 434 function of time. The two, time dependent, signals increase from the point where the light was 435 switched on (100 s after the beginning of the measurement) until the light exposure was ended, 436 following a biexponential function. The expected mechanism should be given by a first-degree 437 reaction that follows a mono-exponential function. The fit carried out on the time dependent 438 EPR signal showed, contrary to the expectations, a biexponential growth. This can be explained 439 by considering the recombination processes that take place during the light excitation of the 440 sample. The observed EPR signal is generated by holes, which appear during the light exposure 441 of the solar cell. As obtained from the biexponential fit (see Tables S2), the rates at which 442 electrons are generated by the pristine solar cell $(12.7 \times 10^{-3} \text{ s}^{-1} \text{ and } 1.27 \times 10^{-3} \text{ s}^{-1})$ are higher 443 than the ones observed for the IM doped cell ($8.446 \times 10^{-3} \text{ s}^{-1}$ and $1.19 \times 10^{-3} \text{ s}^{-1}$). The total 444 445 concentration of holes generated in the doped solar cell is 1.5 times higher after 25 minutes of 446 irradiation. This implicitly means that the doped solar cell generates more electrons transferred to the conduction band. After the light exposure stopped, the EPR signal decayed slowly but it 447 448 did not reach the initial intensity. The recombination process in the pristine solar cell is much stronger, 20% of the light generated paramagnetic centers recombine. The IM doped solar cell 449 450 shows a much slower recombination rate, with a signal loss of only 8%. This indicates that the doped cell has a much better stability than the pristine one. 451

452 *3.2. Solar cells measurements*

453 To evaluate how the IM⁺ insertion influences the performance of solar cells, we fabricated a total number of 181 devices, containing different doping concentrations for the active layer. 454 All photovoltaic parameters are presented as arithmetic average between forward and reverse 455 values obtained from the measurements for each cell, depicted in Table 5. The dynamic 456 hysteretic effects are also shown as the hysteresis index Hi, defined previously as the ratio 457 between the areas found between reverse (R), forward (F) scans [How measurement protocols 458 influence the dynamic J-V characteristics of perovskite solar cells: Theory and experiment], 459 and the total integrated power output of both reverse and forward scans in the range of 0 to V_{oc} 460 value. Each parameter is plotted as a function of the IM doping for the champion and average 461 462 values measured and shown in Figure 11.

Table 5. Photovoltaic parameters as average values between forward and reverse values and for all devices with the same perovskite composition.

| X | Voc | J _{SC} | FF | Rs | Rsh | Hi | PCE |
|-------------|-------------|-----------------------|-----|-------------------------|-------------------------|-----|------|
| (IM) | (V) | (mA/cm ²) | (%) | $(\Omega \text{ cm}^2)$ | $(\Omega \text{ cm}^2)$ | (%) | (%) |
| 0 | 0.999 | 17.4 | 54 | 19 | 1671 | 4.5 | 9.33 |
| 0.02 | 0.992 | 19.0 | 47 | 26 | 644 | 5.6 | 8.80 |
| 0.04 | 0.992 | 17.0 | 53 | 16 | 1150 | 6.5 | 8.80 |
| 0.05 | 0.973 | 16.0 | 51 | 18 | 1056 | 7.2 | 7.89 |
| 0.06 | 0.976 | 17.2 | 53 | 16 | 1539 | 5.9 | 8.92 |
| 0.07 | 0.997 | 15.7 | 53 | 16 | 742 | 6.6 | 8.38 |
| 0.08 | 0.975 | 15.3 | 52 | 16 | 1180 | 6.5 | 7.75 |
| 0.10 | 0.956 | 15.4 | 50 | 17 | 1429 | 7.2 | 7.35 |
| 0.20 | 0.885 | 13.23 | 47 | 27 | 1059 | 6.3 | 5.45 |

Analyzing the results of solar cells measurements, we note that the efficiency is slightly 465 lower by doping with IM. This result was expected since the high crystallinity of the devices is 466 mandatory for good PCE [Dominant effect of the grain size of the MAPbI3 perovskite controlled by 467 the surface roughness of TiO2 on the performance of perovskite solar cells DOI: 468 10.1039/d0ce00169d] and in our case a slight decrease in crystallinity was observed during the 469 process of doping with IM. Among the cells containing IM, the highest efficiency is achieved 470 for those with IM6, with PCE of 8.92%. This is attributed to the maximum value reached by 471 the V_{oc}, since the values for J_{sc} and FF are almost the same. We associate this effect to the 472 improved film quality, in good agreement with the previous measurements (XRD, SEM and 473 AFM). However, once the doping exceeds 6% concentration, the efficiency begins to decrease 474 475 and the detrimental effect of IM begins to reveal, due to the pinholes occurrence and the 476 different perovskite morphology.



479 Figure 11. Photovoltaic parameters for solar cells with IM doped and undoped perovskite, champion
480 cells and average values a) PCE b) Jsc, c) Voc and d) FF.

Therefore, the IM doping for this composition is beneficial until a certain value (6%), any increase of this value resulted in decreased perovskite film quality having as consequences low PCE values. Moreover, having only a slight drop of the PCE, being aware of the importance of stability and the XPS and EPR data which suggested that IM insertion emerged in more stable devices, we further performed the stability measurements for IM modified devices.

486 3.3. Solar cells stability measurements

The stability of the solar cells was monitored by performing photovoltaic measurements on 10 cells (5 pristine and 5 with IM6 respectively), over 2000 hours shelf storage in a low humidity environment (<10%), and the results are presented in Figure 12.



490 491

Figure 12. Solar cells efficiency over 2000 h shelf storage.

The pristine devices degrade faster compared with their IM6 doped counterparts. After 493 2000 h, IM6 devices retain, on average 70% of their original efficiency while the undoped cells 494 495 preserve only 40% of their initial PCE or even became short-circuited, corresponding to a twofold increase of the degradation speed. This indicates that the perovskite with 6% IM is more 496 497 stable compared with MAPI, the $MA_{0.94}IM_{0.06}PbI_{2.6}Cl_{0.4}$ structure being more resilient to degradation. 498

4. Conclusions 499

500

Summarizing, we have studied the effect of imidazolium doping at the A-site of the 501 502 MAPbI_{2.6}Cl_{0.4} perovskite. We calculated the new tolerance factor which revealed that the 3D 503 structure can be maintained only at maximum of 20% added IM. For solar cells, we find an optimum doping percent of 6%. Even though for our devices shows a slightly lower efficiency 504 505 than that of the pristine, undoped perovskites, we prove that the stability for doped devices increases over time. EPR studies have shown that IM doping generates more charges in doped 506 films, and this effect correlated with better film compactness leads to a more efficient capture 507 of the generated charges and a lower recombination rate for these cells. At the same time XPS 508 509 measurements revealed a considerable reduced iodine migration in doped perovskite films, which is confirmed by the stability measurements of solar cells over 2000 hours. Our work 510 511 confirms once again that efficiency is not everything, especially if sacrificing a small percentage of efficiency improves the stability of perovskite film. 512

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Figure S1 Schematic mesoscopic solar cell structure.

- **Table S1.** Tolerance factors calculated according to reference [42] for MA_{1-x}IM_xPbI_{2.6}Cl_{0.4},
- 663 with x ranging from 0 to 1.

| x | t |
|------|--------|
| 0 | 0.9677 |
| 0.02 | 0.9706 |
| 0.04 | 0.9736 |
| 0.05 | 0.9751 |
| 0.06 | 0.9766 |
| 0.07 | 0.9780 |
| 0.08 | 0.9795 |
| 0.10 | 0.9825 |
| 0.20 | 0.9973 |
| 0.25 | 1.0047 |
| 0.5 | 1.0418 |
| 0.75 | 1.0789 |
| 1 | 1.1159 |

665 Table S2.

| Model | ExpGro2 |
|-----------------|--|
| Equation | $y = A1^* exp(x/t1) + A2^* exp(x/t2) + y0$ |
| Plot | Pristine |
| у0 | 0.23814 ± 0.00145 |
| A1 | -0.13656 ± 0.01037 |
| t1 | -78.74557 ± 5.04077 |
| A2 | -0.20605 ± 8.39335E-4 |
| t2 | -787.31457 ± 17.24113 |
| Reduced Chi-Sqr | 2.07214E-5 |
| R-Square (COD) | 0.98998 |
| Adj. R-Square | 0.98997 |

| Model | ExpGro2 |
|-----------------|--|
| Equation | $y = A1^{*}exp(x/t1) + A2^{*}exp(x/t2) + y0$ |
| Plot | IM |
| у0 | 0.34677 ± 0.00207 |
| A1 | -0.14885 ± 0.00387 |
| t1 | -118.38345 ± 5.96608 |
| A2 | -0.28592 ± 0.00176 |
| t2 | -841.06909 ± 20.82076 |
| Reduced Chi-Sqr | 2.63489E-5 |
| R-Square (COD) | 0.99411 |
| Adj. R-Square | 0.9941 |

| Model | ExpDec2 |
|-----------------|--|
| Equation | $y = A1^{*}exp(-x/t1) + A2^{*}exp(-x/t2) + y0$ |
| Plot | Pristine |
| у0 | 0.16128 ± 8.05162E-4 |
| A1 | 8.46466E14 ± 4.65305E15 |
| t1 | 38.83496 ± 5.72923 |
| A2 | 26.93572 ± 56.97753 |
| t2 | 200.21708 ± 53.09653 |
| Reduced Chi-Sqr | 2.15192E-5 |
| R-Square (COD) | 0.783 |
| Adj. R-Square | 0.78242 |