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Enhanced stability and bandgap tuning of α -[HC(NH₂)₂]PbI₃ Hybrid Perovskite by Large Cation Integration.

Antonin Leblanc,^a Nicolas Mercier,^{*a} Magali Allain,^a Jens Dittmer,^b Thierry Pauporté,^c Vincent Fernandez,^d Florent Boucher,^d Mikael Kepenekian,^e Claudine Katan^{*e}

^a MOLTECH-ANJOU, UMR-CNRS 6200, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France.

^b Institut des Molécules et Matériaux du Mans, CNRS UMR 6283, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans cedex 9, France

^c Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), 11 rue P. et M. Curie, F-75005 Paris, France.

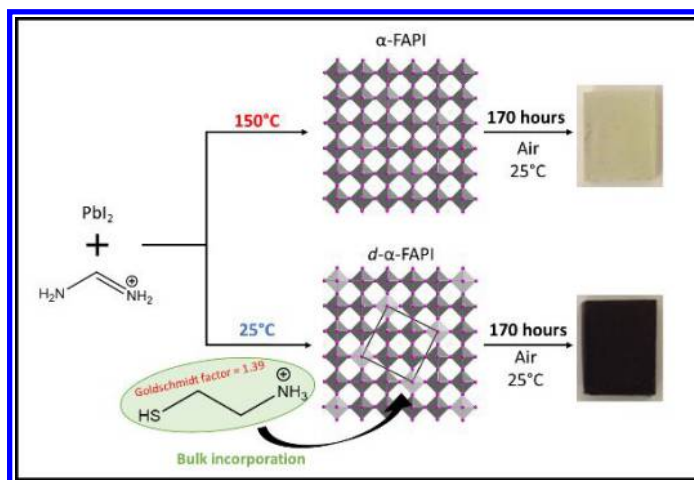
^d Institut des Matériaux Jean Rouxel, UMR-CNRS 6502, Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

^e Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France

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ABSTRACT

We report room temperature synthesis of lead and iodide deficient α -[HC(NH₂)₂]PbI₃ perovskites (abbreviated d - α -FAPI, FA⁺ = formamidinium), owning the general formula



(A',FA)_{1+x}[Pb_{1-x}I_{3-x}] (with A' = hydroxyethylammonium (HEA⁺) or thioethylammonium

(TEA⁺) cations, $0.04 \leq x \leq 0.15$). These materials retain a 3D character of their perovskite network despite incorporation of large HEA⁺ or TEA⁺ cations, demonstrating that the Goldschmidt tolerance factor can be bypassed. We found that thin films of (TEA,FA)_{1+x}[Pb_{1-x}I_{3-x}] ($x = 0.04$ and 0.13) show exceptional α -phase stability under ambient conditions, one order of magnitude higher compared to α -FAPbI₃ and α -(Cs,FA)PbI₃ thin films. *d*- α -FAPbI₃ phases are shown to maintain a direct bandgap, which increases monotonously for x ranging from 0 up to 0.20, with characteristics of a p-type semiconductor for low concentrations of vacancies ($x \leq 0.13$) and n-type for larger ones. They offer an alternative to reach methylammonium- and bromine-free stable α -FAPbI₃ type phase, and open new avenues in the field of perovskite solar cells, up to bandgap tuning desirable for tandem solar cells.

INTRODUCTION

Since 2012, perovskite based solar cells (PSCs) have shown an impressive potential, combining advantages of low-temperature thin film processing (cost process less than half of the price of c-Si solar cell technology),^{1,2} a high power conversion efficiency (PCE) certified up to 23.7%,^{3,4} and the possibility of recycling the solar cells.^{5,6} However, the well-known (CH₃NH₃)PbI₃ hybrid perovskite (abbreviated MAPbI₃, with MA⁺ = methylammonium) firstly used in PSC has shown a fast degradation under air exposure that hinders market development.⁷ Consequently, a chemical approach has been applied consisting in substituting the MA⁺ cation with a less hydrophilic one, presenting a Goldschmidt tolerance factor in the 0.8-1.0 range suitable for the perovskite phase.⁸ Formamidinium (FA⁺) has been considered as a good candidate since the Goldschmidt factor of FAPbI₃ (called FAPbI₃), is close to 1.0.⁸ Unfortunately, the perovskite α -FAPbI₃

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3 phase, which possesses a better thermal stability and a more suitable bandgap than MAPI,⁹
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5 is only synthesized and is thermodynamically stable beyond 150°C. When cooling down
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7 to room temperature under ambient atmosphere, α -FAPbI₃ rapidly transforms into δ -FAPbI₃,
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9 an undesirable polymorph phase that does not present a perovskite architecture nor
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11 photoactivity.¹⁰ In order to slow down this α -to- δ phase transformation, a double cation
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13 strategy was first developed. This chemical approach consists of the α -phase stabilisation
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15 by mixing two materials possessing a large and a small Goldschmidt tolerance factors,
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17 leading to an alloy which owns a balanced factor comprised between the suitable range
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19 [0.8 - 1.0]. The resulting two archetype compounds are Cs_{0.15}FA_{0.85}PbI₃ and
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21 MA_{0.20}FA_{0.80}PbI₃.^{11,12} This strategy was successful as the α -to- δ phase transformation was
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23 observed after a longer time (air condition) than with α -FAPbI₃, and improved efficiencies
24
25 for solar cells were also achieved. Subsequently, other combinations of multiple cations
26
27 and mixed halide were employed, leading to the most stable and efficient alloys α -
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29 (Rb/Cs/MA)_{0.20-0.25}FA_{0.75-0.80}Pb(I_{0.85}Br_{0.15})₃, regularly exceeding 20% solar cells.¹³⁻²⁰
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31 However, despite the beneficial effects of the presence of MA⁺ and Br⁻ ions on the α -phase
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33 purity, crystallinity, stability and on solar cell efficiencies, both volatile MA⁺ cation and
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35 Br⁻ halide induce thermal degradation and an unsuitable blue-shift of the bandgap.²¹
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37 Moreover, from a chemical point of view, this multi-cations alloying strategy is still sorely
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39 limited by the choice of the cations that possess a suitable size to keep a 3D perovskite
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41 architecture.
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49 Recently, we have reported unprecedented lead and iodide deficient hybrid perovskite
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51 materials (*d*-HP family), owning a general formulation (A')_{3.48x}(A)_{1-2.48x}[Pb_{1-x}I_{3-x}], where
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53 A = MA⁺ and A' = HEA⁺ (hydroxyethylammonium HO-(CH₂)₂-NH₃⁺).²² The resulting
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3 phases, named *d*-MAPI, present a 3D perovskite corner-shared $\text{Pb}_{1-x}\text{I}_{3-x}$ ($x = 0$ to 0.20)
4 network, which can be described as a lead and iodide deficient PbI_3 MAPI network. A
5 slightly improved air stability has been demonstrated for this *d*-MAPI phases as compared
6 to MAPI.²² More recently, Diau *et al.* have prepared the tin analogue (*d*-(MA)SnI₃) which
7 also shows good air stability.²³ This superior air stability was also observed for the *hollow*
8 hybrid perovskites named (A',A)MI₃ (A' = en²⁺ = ethylenediammonium, A = MA⁺/FA⁺, M
9 = Pb²⁺/Sn²⁺) reported by the Kanatzidis' group.²⁴ When A = FA⁺, a series of *hollow*
10 perovskites are obtained: (FA)_{1-x}(en)_xPb_{0.7x}I_{3-0.4x}. However, they are synthesized at
11 temperatures over 100 °C, as the α -FAPb phase, and no thin film preparation (and so no
12 thin film stability test) of these *hollow- α* -FAPb phases has been reported.²⁴

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26 In this study, we report the room temperature synthesis of a family of lead and iodide
27 deficient α -FAPb (*d- α* -FAPb) hybrid perovskites. These 3D perovskites incorporate the
28 formamidinium cation and a larger size cation, either the hydroxyethylammonium (HEA⁺,
29 *d- α* -FAPb-**H_x** compounds) or the thioethylammonium (TEA⁺, *d- α* -FAPb-**T_x** compounds)
30 monocation. The general formula of these materials is (FA,A')_{1+x}[Pb_{1-x}I_{3-x}] with A' = HEA⁺
31 or TEA⁺. Crystals of *d- α* -FAPb have been grown, allowing the selection and structure
32 determination of one composition, (HEA)_{0.406}(FA)_{0.698}[Pb_{0.896}I_{2.896}] ($x = 0.104$, written *d- α* -
33 FAPb-**H_{0.104}**), which revealed the 3D nature of the perovskite network. Several materials
34 have been also prepared as pure crystallized powder phases, two *d- α* -FAPb-**H_x** (with $x =$
35 0.13 and $x = 0.15$, here abbreviated **H_{0.13}**, and **H_{0.15}**), and one *d- α* -FAPb-**T_x** ($x = 0.04$,
36 abbreviated **T_{0.04}**), as well as thin films (**H_{0.13}**, **H_{0.15}**, **T_{0.04}** and also **T_{0.13}** ($x = 0.13$)).
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3 visible absorption and X-ray photoelectron spectroscopy (XPS) measurements. Moreover,
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5 the analysis has been completed by computational DFT investigations. Besides the fact that
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7 these α -FAP_x type phases can be synthesized at room temperature, we show that the
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9 stability of the α phase at room temperature and under ambient condition (thin films, case
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11 of d - α -FAP_x-T_x materials) is exceptionally improved compared to both α -FAP_x and α -
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13 Cs_{0.15}FA_{0.85}PbI₃ reference materials.
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19 RESULTS AND DISCUSSION

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21 Crystals of d - α -FAP_x have been obtained at room temperature by slow liquid-gas diffusion
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23 process using aqueous hydroiodic acid and ethanol as solvent and anti-solvent, respectively
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25 (more details in Supporting Information -I.a-). These crystals have a cross shape (Figure
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27 **1a**), and depending on experimental conditions they can be black or dark red. It is also
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29 worth noting that no yellow crystals of δ -FAP_x were co-crystallized. For all x values ,
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31 single-crystal X-ray diffraction analysis of d - α -FAP_x-H_x has revealed room temperature
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33 tetragonal unit cells ($a = b = 14.471 \text{ \AA}$, $c = 6.448 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 1350.2 \text{ \AA}^3$),
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35 slightly larger than the previously reported d -MAP_x unit cell (also obtained at room
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37 temperature: $a = b = 14.312 \text{ \AA}$, $c = 6.366 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 1303.9 \text{ \AA}^3$).²² This can be
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39 correlated to the effective radius of FA⁺ (253 pm) which is larger than the one of MA⁺ (217
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41 pm).²⁵ The structure of the d - α -FAP_x-H_x was studied from one single crystal selected
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43 among many other. The d - α -FAP_x-H_x phase crystallises at room temperature into the P4/m
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45 space group (see S.I. IV, Table S7). Despite several attempts at different temperatures (100-
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47 293K range), the X-ray study has only allowed the determination of the inorganic network.
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54 This can be partly explained at room temperature by a dynamical disorder of both HEA⁺
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3 and FA⁺ organic cations, as revealed by solid state NMR experiments (see below). At lower
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5 temperature, this may be explained by a statistical disorder. Structural refinements finally
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7 led to a Pb_{4.48}I_{14.48} formula per unit cell for the inorganic part. The structure can be
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9 described from a main 3D Pb₄I₁₄ perovskite network of corner-sharing PbI₆ octahedra with
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11 a 3D arrangement which generates channels along the *c* axis (Figure 1b). These channels
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13 are half filled with extra Pb²⁺ and I⁻ ions, located in (0, 0, 0) and (0, 0, 0.5), respectively.
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15 To highlight the lead and iodide deficiency of this 3D perovskite network, the Pb_{4.48}I_{14.48}
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17 formula should be written as Pb_{0.896}I_{2.896} or Pb_{1-x}I_{3-x} with $x = 0.104$ (*d*-α-FAPI-**H**_{0.104}). The
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19 general formulation of the *d*-α-FAPI-**H**_{*x*} phases is (HEA)_{3.9*x*}(FA)_{1-2.9*x*}[Pb_{1-x}I_{3-x}] or
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21 (HEA,FA)_{1+x}[Pb_{1-x}I_{3-x}] according to different chemical analyses of crystals and powders
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23 (see below and S.I.) and therefore the formula of this studied crystal is
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25 (HEA)_{0.406}(FA)_{0.698}[Pb_{0.896}I_{2.896}]. Thus, the lead and iodide deficient *d*-α-FAPI phase can
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27 be described from the α-FAPI phase through a substitution of *x* (PbI)⁺ units by *x* organic
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29 cations, HEA⁺ or FA⁺. In the case of $x = 0.2$ (Pb_{0.8}I_{2.8} or Pb₄I₁₄ network), all Pb²⁺ and I⁻ ions
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31 along the *c* direction have been substituted by organic cations leading to empty channels.
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33 When $0 \leq x \leq 0.2$ (case of the studied crystal *d*-α-FAPI-**H**_{0.104}), the X-ray analysis shows
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35 that channels contain Pb²⁺ and I⁻ anions as well as organic cations. Consequently, one
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37 hypothesis is a partial filling of channels by Pb²⁺ and I⁻. Another hypothesis is that
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39 intermediate values of *x* may correspond to a limited number of empty channels in the
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41 structure (see below the model structures used for calculations). Finally, it must be noted
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43 that the poor quality of crystals of *d*-α-FAPI-**T**_{*x*} precluded their X-ray single crystal
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45 analysis.
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3 From the crystal structure analysis of the anhydrous iodide salts of
4 hydroxyethylammonium (HEAI) and thioethylammonium (TEAI) which have revealed
5 that HEA⁺ and TEA⁺ cations adopt a curving shape (S.I. Tables S8 and S9), we estimated
6 the effective radius of HEA⁺ (3.44 Å) and TEA⁺ (4.14 Å) according to the model proposed
7 by Kieslich *et al.*²⁵ Thus, the Goldschmidt factors of the hypothetical (HEA)PbI₃ and
8 (TEA)PbI₃ perovskites were calculated as 1.24 and 1.39, respectively. These values are far
9 from the expected 0.8-1.0 range usually necessary to stabilize the 3D ABX₃ perovskite.⁸
10 However, the 3D perovskite structures of α -FAPI type prepared in this work (*d*- α -FAPI
11 phases) have been stabilized despite the incorporation of these HEA⁺ / TEA⁺ cations (see
12 below). This is explained by the presence of (PbI)⁺ vacancies in the 3D network. This
13 family of compounds (*d*-HP) shows that it is possible to circumvent the geometrical
14 Goldschmidt factor and to obtain 3D hybrid perovskites even using larger R-NH₃⁺ organic
15 cations. Moreover, the integration of HEA⁺/TEA⁺ cation allows the synthesis at room
16 temperature of the α -FAPI type network (*d*- α -FAPI) while α -FAPI reference is prepared
17 only at temperature over 150 °C.
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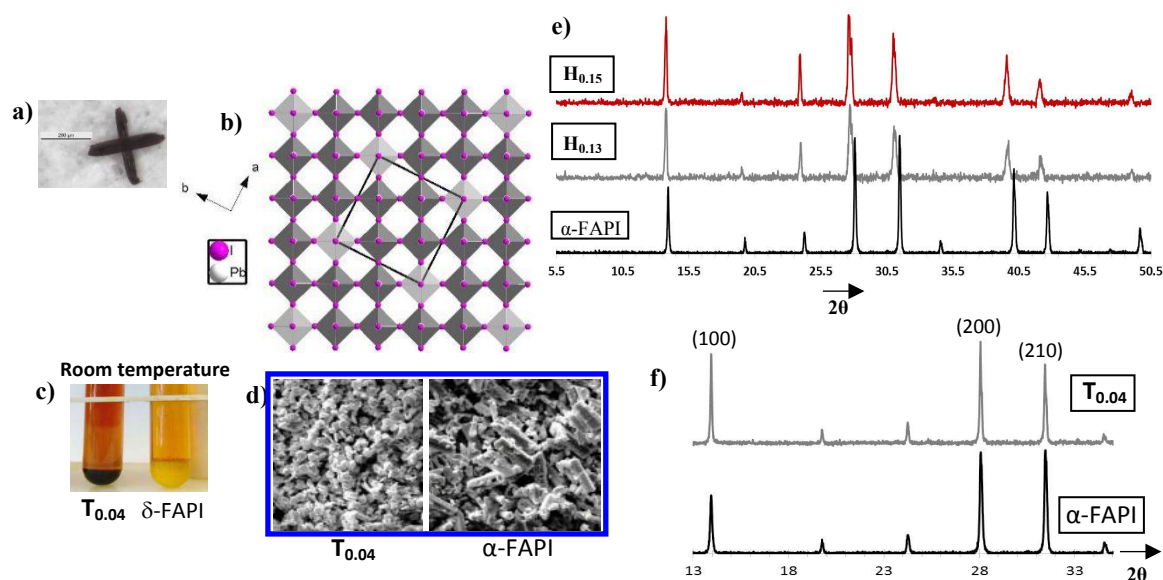


Figure 1. *a)* Cross-shaped crystals of *d*-α-FAPI. *b)* View along the *c* axis of the tetragonal unit cell (black square) of the structure of $(\text{HEA,FA})_{1.104}[\text{Pb}_{0.896}\text{I}_{2.896}]$ showing the lead and iodide deficient perovskite network (dark grey octahedra : full Pb^{2+} and I sites occupancy, light grey octahedra: half Pb^{2+} and I sites occupancy). *c)* Photography of $\text{T}_{0.04}$ and δ -FAPI powders synthesized at room temperature; *d)* SEM images of crystallized powders of $\text{T}_{0.04}$ and α -FAPI; *e)* XRD patterns of $\text{H}_{0.13}$, $\text{H}_{0.15}$ and α -FAPI powders showing the shift of lines towards low angles for $\text{H}_{0.13}$ and $\text{H}_{0.15}$; *f)* XRD patterns of $\text{T}_{0.04}$ and α -FAPI powders highlighting the (100), (200) and (210) diffraction lines.

Powders of *d*-α-FAPI- H_x and *d*-α-FAPI- T_x were prepared by a fast precipitation method at room temperature. Increasing amounts of hydroxyethylamine/FAI/ PbI_2 or thioethylamine/FAI/ PbI_2 were dissolved at room temperature into aqueous hydroiodic acid under ultrasonication until the saturation was reached. Then, the saturated solution was

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3 poured into ethyl acetate, immediately leading to the precipitation of a powder (more
4 details in S.I. I.b). Pure *d*- α -FAPI- \mathbf{H}_x phases with $x = 0.13$ ($\mathbf{H}_{0.13}$) and $x = 0.15$ ($\mathbf{H}_{0.15}$), as
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6 well as one pure phase of *d*- α -FAPI- \mathbf{T}_x with $x = 0.04$ ($\mathbf{T}_{0.04}$), were obtained and fully
7
8 characterized. We also prepared the δ -FAPI by starting from PbI_2 and FAI as reagents, and
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10 also synthesized α -FAPI compound by heating the δ -FAPI powder at 155°C during 30 min.
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12 A color change then occurs from yellow to black characterizing the δ -FAPI to α -FAPI
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14 phase transition. Despite our best efforts to precipitate pure phases with compositions in
15
16 the $x = 0$ - 0.20 range, only one composition could be obtained for *d*- α -FAPI- \mathbf{T}_x ($\mathbf{T}_{0.04}$) while
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18 two distinct compositions ($\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$) were obtained with HEA^+ . In all other
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20 experiments, the yellow δ -FAPI was crystallized as impurity. Figure 1c (zoomed Figure
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22 S7) shows a photography of δ -FAPI and $\mathbf{T}_{0.04}$ precipitated powders. δ -FAPI powder has a
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24 typical yellow color while the $\mathbf{T}_{0.04}$ powder is black, showing that another phase is obtained
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26 when a small amount of TEA^+ is incorporated in the system, which will be proved to be a
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28 α -FAPI type phase (*d*- α -FAPI). Furthermore, it is worth noting that the morphology of α -
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30 FAPI and $\mathbf{T}_{0.04}$ micrometer-size crystals (obtained by the precipitation method) are very
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32 different, as shown by scanning electron microscopy images (Figure 1d, zoomed Figure
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34 S8). Indeed, the elongated shape of α -FAPI crystals is the consequence of the preferential
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36 growth along the PbI_3^- chain direction of the initial δ -FAPI compound,¹⁰ while a cube shape
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38 is observed for $\mathbf{T}_{0.04}$ crystals proving that the cubic α -FAPI type network was directly
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40 obtained. $\mathbf{H}_{0.13}$, $\mathbf{H}_{0.15}$ and $\mathbf{T}_{0.04}$ samples have been fully characterized, first by energy
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42 dispersive X-ray spectroscopy (EDX) allowing the determination of the I/Pb atomic ratios.
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44 Considering the inorganic network $[\text{Pb}_{1-x}\text{I}_{3-x}]$ as found in the *d*-MAPI phases
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46 ($\text{HEA,MA})_{1+x}[\text{Pb}_{1-x}\text{I}_{3-x}]$,²² and in this studied crystal $\mathbf{H}_{0.104}$ ($\text{Pb}_{0.896}\text{I}_{2.896}$ network, $x = 0.104$),
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3 the measured I/Pb atomic ratios gave $x = 0.13$ for $\mathbf{H}_{0.13}$, $x = 0.15$ for $\mathbf{H}_{0.15}$, and $x = 0.04$ for
4 $\mathbf{T}_{0.04}$ (Figures S1, S8, and Tables S3, S6). Moreover, ^1H nuclear magnetic resonance
5 spectroscopy (NMR) in solution led to determine the following HEA^+/FA^+ and TEA^+/FA^+
6 molecular ratios: $\text{HEA}^+/\text{FA}^+ = 0.81$ for $\mathbf{H}_{0.13}$ and 1.13 for $\mathbf{H}_{0.15}$, and $\text{TEA}^+/\text{FA}^+ = 0.13$ for
7 $\mathbf{T}_{0.04}$ (Figures S2-S6, S9-11). The following formulations were thus deduced:
8 $(\text{HEA})_{0.51}(\text{FA})_{0.62}[\text{Pb}_{0.87}\text{I}_{2.87}]$ ($\mathbf{H}_{0.13}$) and $(\text{HEA})_{0.60}(\text{FA})_{0.55}[\text{Pb}_{0.85}\text{I}_{2.85}]$ ($\mathbf{H}_{0.15}$), consistent
9 with the general formulation of $(\text{HEA})_{3.9x}(\text{FA})_{1-2.9x}[\text{Pb}_{1-x}\text{I}_{3-x}]$, with $x = 0.13$ and $x = 0.15$;
10 and $(\text{TEA})_{0.12}(\text{FA})_{0.92}[\text{Pb}_{0.96}\text{I}_{2.96}]$ ($\mathbf{T}_{0.04}$, $x = 0.04$). All these compositions were finally
11 confirmed by elemental analysis (Tables S1, S2, S4, and S5). The purity of all these
12 crystallized powders was also verified by powder X-ray diffraction (XRD) analysis. The
13 XRD patterns of the yellow δ -FAPI and the black α -FAPI powders (Figures S12 and S13)
14 perfectly fit with their theoretical XRD patterns, calculated from both known δ -FAPI and
15 α -FAPI structures (δ -FAPI: hexagonal $\text{P6}_3\text{mc}$, $a = b = 8.7 \text{ \AA}$, $c = 7.9 \text{ \AA}$; α -FAPI: cubic Pm-
16 3m , $a = 6.362 \text{ \AA}$ for).^{10,26}

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35 As regards $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ powders, their XRD patterns are in good agreement with the
36 calculated XRD pattern from the single crystal data of $(\text{HEA,FA})_{1.104}[\text{Pb}_{0.896}\text{I}_{2.896}]$ (Figure
37 S14). In Figure 1e, diffractograms of $\mathbf{H}_{0.13}$, $\mathbf{H}_{0.15}$ and α -FAPI powders are provided.
38 Compared to α -FAPI, a slight shift of most peaks of $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ towards lower angles
39 is observed (see also zoom in Figure S15). This phenomenon, revealing a slight increase
40 of unit cell parameters through the substitution process of $(\text{PbI})^+$ units by organic cations,
41 has been already observed in the case of d -MAPI phases $(\text{HEA,MA})_{1+x}[\text{Pb}_{1-x}\text{I}_{3-x}]$.²² Three
42 peaks of low intensity which were expected at low 2θ angles (6.2° , 8.7° , 12.3°) are absent
43 in the XRD patterns of $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ (Figure 1e and Figure S14 -theoretical XRD pattern-
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3). These lines are assigned to (1 0 0), (1 1 0) and (2 0 0) planes of the tetragonal unit cell
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5 (a = 14.312 Å, c = 6.366 Å) typical of the *d*-HP phase²² (see Figure 1b). The fact that these
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7 lines are not observed could be explained by a preferential orientation phenomenon of (0
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9 0 l) type, but most probably the smaller unit cell observed is resulting of a non-ordered
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11 distribution of defaults (lead and iodide vacancies) as observed in *hollow* structures based
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13 on ethylenediammonium cations.²⁴ Unlike the *d*- α -FAPI- \mathbf{H}_x phases, the XRD pattern of
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15 $\mathbf{T}_{0.04}$ does not present significant shifts compared to the α -FAPI XRD one (Figures 1f, S16).
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17 This may be explained by the low incorporation of TEA⁺ cations into this $\mathbf{T}_{0.04}$ phase (x=
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19 0.04, TEA/FA= 0.13). Nevertheless, we can notice differences for several diffraction peak
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21 intensities. Thus, the intensities I(100)/I(200) ratio ((100) line at 13.9° and (200) line at
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23 28.0°) appears higher in $\mathbf{T}_{0.04}$ than in α -FAPI, and this cannot be explained by a preferential
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25 orientation phenomenon. We also notice that I(210) ((210) line at 31.4°) is lowered in $\mathbf{T}_{0.04}$
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27 compared to α -FAPI. This feature is probably the consequence of a slight structural
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29 modification involved by the incorporation of TEA⁺ in $\mathbf{T}_{0.04}$. Moreover, this phenomenon
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31 is also observed when materials ($\mathbf{T}_{0.04}$, $\mathbf{T}_{0.13}$, and α -FAPI) are prepared as thin films (see
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33 below).
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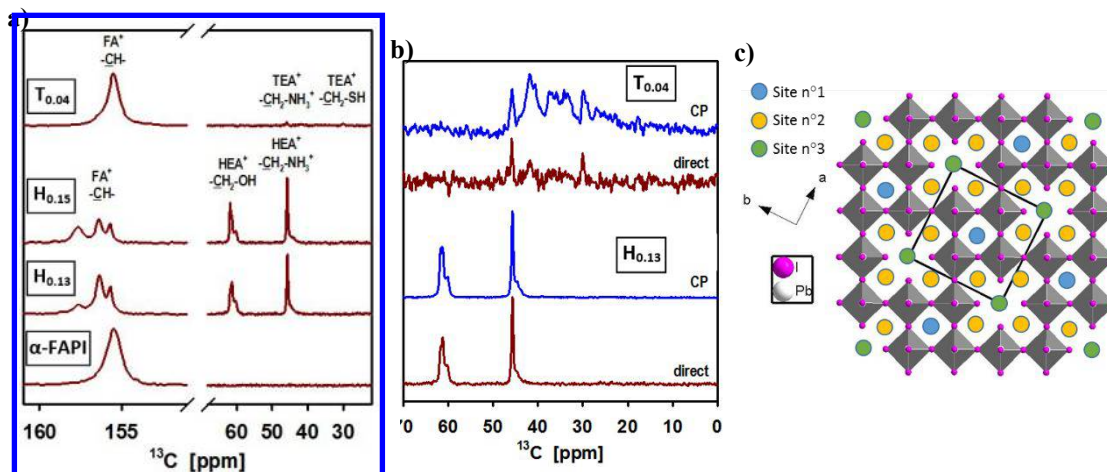


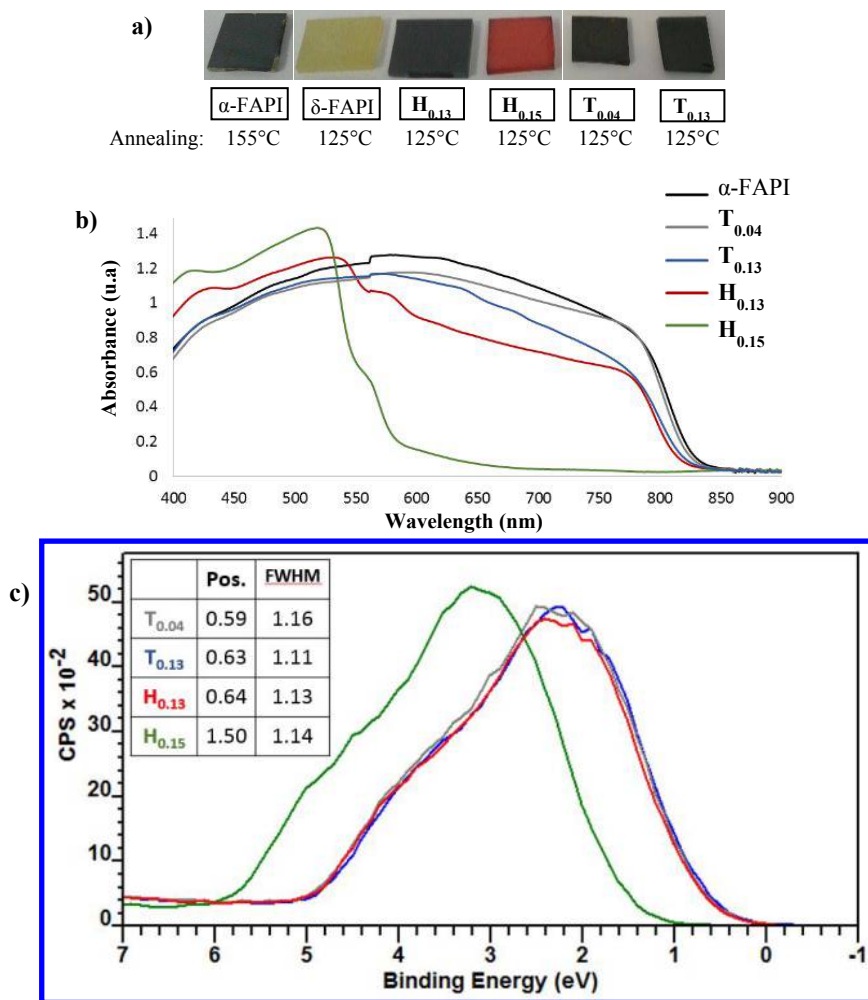
Figure 2. *a)* Direct excitation solid state NMR spectra of α -FAPI, $H_{0.13}$, $H_{0.15}$, and $T_{0.04}$, scaled according to the number of scans. *b)* The upfield region of the direct excitation spectra (red) of $H_{0.13}$ and $T_{0.04}$ compared to the corresponding cross polarization spectra (blue). Arbitrary scale. *c)* View along the c axis of the tetragonal unit cell (black square) of a hypothetical structure of d - α -FAPI with $x = 0.20$ (resulting formula of (HEA or TEA, FA) $_{1.2}$ [Pb $_{0.8}$ I $_{2.8}$]). The organic cations are located on the three different crystallographic site $n^{\circ}1$, $n^{\circ}2$ and $n^{\circ}3$ (blue, yellow and green circles, respectively).

^{13}C solid state NMR was used to characterize the organic cations, invisible to XRD, verify their incorporation into the perovskite framework and gain information on their dynamics. While the direct excitation ^{13}C spectrum of α -FAPI shows the expected single signal of the FA^+ carbon (at 155.5 ppm), the materials $H_{0.13}$ and $H_{0.15}$ show two additional signals around 61 and 45 ppm, corresponding to $-\text{CH}_2-\text{OH}$ and of $-\text{CH}_2-\text{NH}_3^+$ of the HEA^+ cation, respectively (Figure 2a). Concerning the FA^+ signal, it shifts upon the insertion of the other cations, similar to MA^+ in d -MAPI phases,²² but also splits into three signals, at identical

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3 positions for $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$. These observations are consistent with the possible occupation
4 of different sites in this lead and iodide deficient perovskite network: three sites for the
5 FA^+ ions, and probably only the sites $n^\circ 2$ and $n^\circ 3$ for HEA^+ ions (see below Figure **2c**).
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7 The least shifted (0.2 compared to 0.9 and 2.2 ppm) signal is here most likely from FA^+ on
8 the site corresponding to the unmodified FAPI structure (site $n^\circ 1$). There is also dispersion
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10 in the HEA^+ signals: both signals in both samples consist of a dominant peak on the
11 downfield side, interpreted as stemming from HEA^+ on the more abundant site $n^\circ 2$, and a
12 broader foot upfield, attributed to HEA^+ on site $n^\circ 3$. The chemical shift range of the latter
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14 contains the shift of HEAI, because the local environment of the carbons on site $n^\circ 3$ is
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16 closer to those in HEAI (Figure S22). The HEA^+ signals show substructures, in particular
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18 the foot of $-\text{CH}_2-\text{NH}_3^+$ on site $n^\circ 3$, indicating that these cations are not all incorporated in
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20 the same way or that there are preferential orientations. In fact, ^{13}C cross-polarization (CP)
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22 spectra of $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ exhibit intense signals compared to α -FAPI showing that the free
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24 rotation of the cations is restrained by the structure (Figure S22). This counts in particular
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26 for the bigger HEA^+ cations. It is thus imaginable that there are preferred orientations that
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28 have lifetimes being long enough that the NMR signals are not fully averaged.
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32 For $\mathbf{T}_{0.04}$, the CH_2 ^{13}C signals of TEA^+ are hardly detectable by a direct excitation
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34 experiment. Their shifts are 45.9 and 30.3 ppm, respectively, different from those of TEAI
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36 (Figure S22). The ^{13}C CP experiment reveals a broad distribution of additional signals in
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38 the CH_2 region (Figure **2b**). Note that this experiment is not quantitative and enhances
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40 signals stemming from less mobile molecules or molecule groups. In the direct excitation
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42 experiment their intensity is so low that they are largely covered by the noise. Nevertheless,
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44 as they are spread over a broader range, they probably constitute the major part of TEA^+ .
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3 (This finding is in contrast to **H_{0.13}** and **H_{0.15}**, where the shapes of the signals acquired with
4 CP and direct excitation are essentially identical, indicating that the dynamics of all HEA⁺
5 is similar (Figure **2b**, **H_{0.13}**.) Incorporated TEA⁺ thus presents in the majority much less
6 rotational mobility compared to the other organic cations (FA⁺, HEA⁺ in **H_{0.13}** and **H_{0.15}**).
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38 **Figure 3. a)** Photography of α -FAPbI₃, δ -FAPbI₃, $H_{0.13}$, $H_{0.15}$, $T_{0.04}$ and $T_{0.13}$ thin films and
 39 their associated temperatures of annealing. **b)** UV-visible absorbance spectra of α -FAPbI₃
 40 (black), $H_{0.13}$ (red), $H_{0.15}$ (green), $T_{0.04}$ (grey), and $T_{0.13}$ (blue) thin films. **c)** XPS spectra of
 41 $H_{0.13}$ (red), $H_{0.15}$ (green), $T_{0.04}$ (grey) and $T_{0.13}$ (blue) thin films, representing the valence
 42 band (VB) energies relative to the Fermi energy ($E_F - E_{VB}$). Inset: respective both energies
 43 (eV) of $E_F - E_{VB}$ (pos.) and FWHM.
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Thin films of d - α -FAP I-H_x and d - α -FAP I-T_x phases as well as α -FAP I were prepared by spin coating at room conditions (see S.I. -I.e- for details). The precursors were added into a solution of dimethylformamide (DMF), and depending on stoichiometries of the reagents, we prepared α -FAP I (PbI $_2$ /FAI: 1/1), $\mathbf{H}_{0.13}$ (PbI $_2$ /FAI/HEAI: 3/3/1), $\mathbf{H}_{0.15}$ (PbI $_2$ /FAI/HEAI: 3/3/2), $\mathbf{T}_{0.04}$ (PbI $_2$ /FAI/TEAI: 3/3/0.5), and contrary to the precipitated powders, we were able to prepare another successfully pure composition $\mathbf{T}_{0.13}$ ($x = 0.13$; PbI $_2$ /FAI/TEAI: 3/3/1.0). The spinning step was followed by an annealing treatment of thin films, at 155°C for α -FAP I and at 125°C for $\mathbf{H}_{0.13}$, $\mathbf{H}_{0.15}$, $\mathbf{T}_{0.04}$, and $\mathbf{T}_{0.13}$. We must notice that the annealing of the FAP I thin film at 125 °C results in the formation of δ -FAP I as a pure phase (yellow thin film). After the annealing step, thin films of α -FAP I , $\mathbf{H}_{0.13}$, $\mathbf{T}_{0.04}$, and $\mathbf{T}_{0.13}$ are black, and red for $\mathbf{H}_{0.15}$ (see Figure 3a).

As for powders, the I/Pb ratio of this films were determined from EDX analysis, leading to $x = 0.13$ ($\mathbf{H}_{0.13}$), $x = 0.15$ ($\mathbf{H}_{0.15}$) (Figure S1, Table S3), $x = 0.04$ ($\mathbf{T}_{0.04}$), and $x = 0.13$ ($\mathbf{T}_{0.13}$) (Figure S8, Table S6). XRD measurements revealed that $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ thin films were obtained as pure phases without the presence of δ -FAP I , α -FAP I or PbI $_2$. The XRD patterns of $\mathbf{H}_{0.13}$ and $\mathbf{H}_{0.15}$ exhibit a shift of most of peaks towards lower angles compared to the lines of α -FAP I , as observed for powders. We also notice that the three very weak peaks at low 2θ angle (6.2°, 8.7°, 12.3°), typical of the tetragonal super-cell of such d -HP (see single crystal study) are observed in the thin film pattern of $\mathbf{H}_{0.15}$ (Figure S17). As in the case of d - α -FAP I-H_x phases, XRD patterns of $\mathbf{T}_{0.04}$ and $\mathbf{T}_{0.13}$ thin films show single phase layers without the presence of PbI $_2$ (Figure S20). This is in contrast with the XRD of α -FAP I thin film (PbI $_2$ is known to be easily generated during the annealing treatment at 155°C -room conditions-) (Figures S18, S19).^{27,28} As observed in the XRD of $\mathbf{T}_{0.04}$ powder and the XRD

of ethylene diammonium (en^{2+}) based *hollow* perovskites $(FA)_{1-x}(en)_x(Pb)_{1-0.7x}(I)_{3-0.4x}$,²⁴ there is no significant shift of diffraction lines in the XRD patterns of $T_{0.04}$ and $T_{0.13}$ thin films compared to the one of α -FAPb phase. However, the specific features observed in the XRD pattern of $T_{0.04}$ powder compared to the one of α -FAPb, which have a higher I(100)/I(200) ratio ((100) line at 13.9° , (200) line at 28.0°) and a lower I(210) intensity ((210) line at 31.4°), are also observed for $T_{0.04}$ and $T_{0.13}$ thin films (Figure S20).

The UV-visible absorption spectra of α -FAPb and $H_{0.13}$, $H_{0.15}$, $T_{0.04}$, $T_{0.13}$ thin films are compared in Figure 3b, and the optical bandgaps were determined from Tauc plot graphs (S.I., Figure S21) leading to 1.50 eV for α -FAPb, 1.51 eV for $T_{0.04}$, 1.53 eV for $H_{0.13}$ and $T_{0.13}$, 1.90 eV for $H_{0.15}$. For $x \leq 0.13$, both the observed blue shift of the bandgap and the decreasing absorption intensity in the 600-800 nm range are proportional to the x value of the perovskite frameworks $[Pb_{1-x}I_{3-x}]$, consistently with earlier findings on *d*-MAPb and *hollow* perovskites.^{22,24} Interestingly, from $x = 0.13$ to $x = 0.15$, the blue shift of the optical bandgap becomes huge. A similar distinctive behaviour is observed using XPS measurements (Figure 3c): the valence band (VB) energies relative to the Fermi energy ($E_F - E_{VB}$) is found almost unchanged for $T_{0.04}$, $T_{0.13}$ and $H_{0.13}$, (0.59 eV, 0.63 eV and 0.64 eV, respectively), whereas it largely increases for $H_{0.15}$ (1.50 eV). Meanwhile, by using low-lying electronic levels of iodine (4d) or lead (4f) as a reference, it is shown that the position of the VB is independent of the composition (S.I., Table S10). Besides, the XPS revealed also two different types of N atom for our *d*- α -FAPb compounds: NH_3^+ group belonging to HEA^+/TEA^+ and NH_2^+ to FA^+ . Note that, as expected, only the N atom of NH_2^+ was observed for α -FAPb (as for examples $T_{0.13}$ and α -FAPb, Figure S23). Moreover, as reported with *d*-MAPb,²² the incorporation of HEA^+/TEA^+ cations has the consequence

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3 to eliminate the formation of Pb(0) under continuous X-ray irradiation compared to the
4 reference α -FAPI (Figure S24).
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8 Furthermore insight into the electronic structure of *d*- α -FAPI compounds has been obtained
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10 by computational investigations based on density functional theory (DFT) including spin-
11 orbit coupling. The starting point for the calculations is the X-ray resolved structure of *d*-
12 α -FAPI-**H**_{0.104} crystal in the P4/m group with partial occupation of (0, 0, 0) and (0, 0, 0.5)
13 lead and iodide sites (see above). As a result of the dynamical motion of the organic cation
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15 evidenced by solid state NMR spectroscopy (see above), no structural information is
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17 available for those cations. Thus, in order to compensate the negative charge of the
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19 inorganic part, Cs⁺ cations have been placed at the center of the vacancies, where FA⁺ are
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21 expected to be located (Figures **4a** & **4b**, and zoomed view Figure S25). As such, the
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23 distinctive nature between the three sites defined in Figure **2c** relies solely on the inorganic
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25 framework. Such a substitution has proved very useful for 3D and layered perovskites,^{30,31}
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27 and holds whenever the molecular frontier orbitals are far above and far below the
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29 conduction (CB) and valence bands, respectively. The first structural model corresponds
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31 to an ideal 3D network with no deficiency of lead and iodide ($x = 0.00$). As expected, it
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33 shows a direct bandgap at A with a computed bandgap energy $E_G = 0.28$ eV (Figure **4a**). It
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35 is well-known that Kohn-Sham DFT dramatically underestimates bandgaps in
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37 semiconductors, although it correctly describes trends. The second structural model
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39 considers the other extreme of the experimentally determined crystal structure where all
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41 the partially occupied sites are taken empty ($x = 0.20$). To retain charge neutrality,
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43 additional Cs⁺ cations are placed at the position of missing Pb atoms, where HEA⁺ or TEA⁺
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45 cations are expected to be inserted. As a result, channels appear with deficiency of lead and
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3 iodide. Despite the extent of the transformation, the resulting band structure (Figure **4b**)
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5 shows remarkably similar features to the pristine system, including a direct bandgap at A.
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7 Meanwhile, the deficiency in lead and iodide atoms leads to two notable differences.
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9 Firstly, the bandgap E_G undergoes a sizeable increase to 0.92 eV, which is in qualitative
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11 good agreement with UV-visible spectra (Figure **3b**). Concomitantly, the bandwidth of
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13 both the valence and conduction bands decreases, which is indicative of increased effective
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15 masses with variations of about +50% and +40% for holes and electrons, respectively.
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17 Naturally, the larger effective masses of charge carriers hinder the optoelectronic properties
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19 of $x = 0.20$ material by lowering the probability to extract charges in the case of solar cells.
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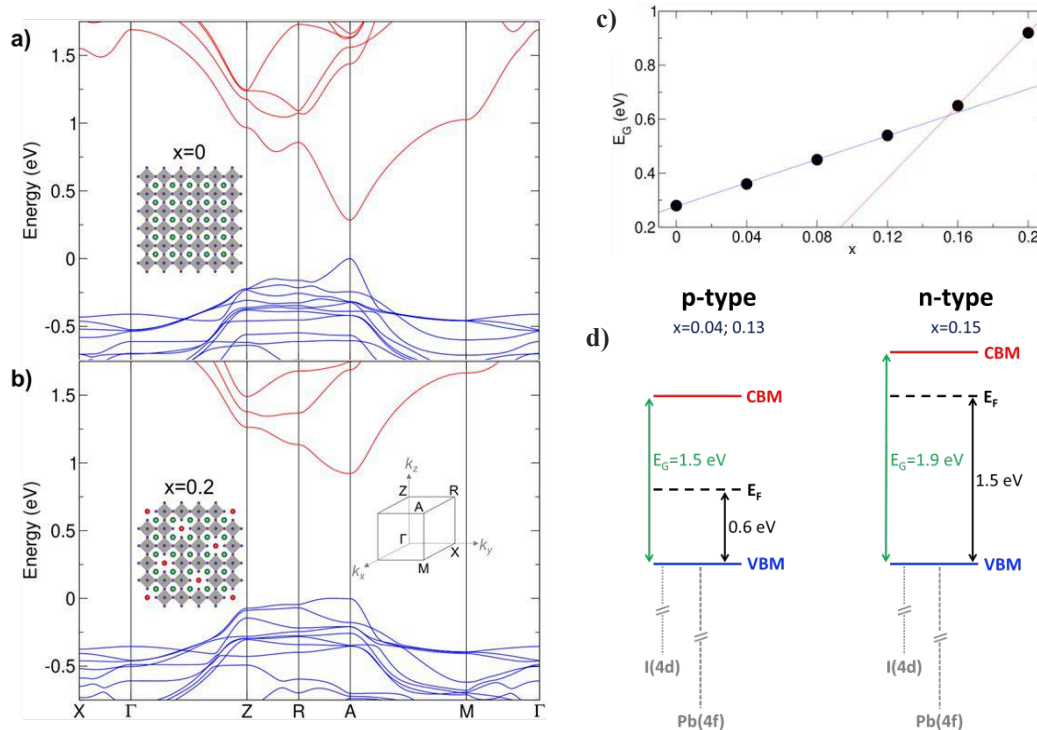


Figure 4. **a)** Electronic band structure for the structure deprived of lead vacancy. **b)** Same for a concentration of vacancies $x = 0.2$. Insets present the structure used for calculations with Pb and I atoms in grey and violet, respectively. Green and red balls show the positions of Cs⁺ cations. Red balls mark the position of PbI vacancies. **c)** Computed bandgap E_G (eV) with respect to the vacancy concentration x . Lines in blue and red correspond to linear fits plotted as guide for the eye. **d)** Schematic evolution of band edges and Fermi level position derived from XPS and DFT results.

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3 To further investigate the impact of composition, we designed a supercell (see S.I., Figure
4 S25). This supercell allows to consider structural defective compositions with $x = 0.00$,
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To further investigate the impact of composition, we designed a supercell (see S.I., Figure S25). This supercell allows to consider structural defective compositions with $x = 0.00$, 0.04, 0.08, 0.12, 0.16 and 0.20 and monitor the evolution of E_G with respect to x (Figure 4c). As expected, a monotonous increase of E_G is obtained between the two end compositions but, two regions can be identified marked by a steep opening of the bandgap for $x > 0.12$ much greater than the one observed for $x \leq 0.12$. (blue and red lines on Figure 4c). Indeed, the linear opening of the bandgap seen for $x > 0.12$ is three times steeper than the one observed for $x \leq 0.12$. This computationally acceleration of bandgap opening for $x > 0.12$ are qualitatively in line with the large variation of E_G and $E_F - E_{VB}$ experimentally observed by UV-visible spectrometry and XPS, respectively, when increasing x from 0.13 to 0.15 (Figure 3b and 3c). In addition, considering the Pb 5d orbitals of as a reference, DFT calculations also confirm that the valence band energy is hardly affected in this range of composition, as the systematic downshift with increasing x value remains below 100meV.

Thus, despite the limitations of the here-presented computational model, in which the x value is monitored by considering an increasing number of infinite channels of defects starting from the experimental structure recorded on the single crystal $(\text{HEA})_{0.406}(\text{FA})_{0.698}[\text{Pb}_{0.896}\text{I}_{2.896}] (\mathbf{H}_{0.104})$, DFT results recover qualitatively both experimental trends obtained on thin films. These experimental and computed results suggest different band diagrams for $x \leq 0.13$ and $x > 0.13$ that are schematically sketched in Figure 4d. It shows that the Fermi level is closer to the VB for the less-deficient ($x \leq 0.13$) compositions, which is characteristic of a p-type semiconductor with positive charges as the majority charge carriers. On the contrary, for $x = 0.15$, the Fermi level is found closer

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3 to the conduction band edge, indicative of a n-type semiconductor. Recently, G. Paul *et al.*
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5 inferred a correlation between electronic conductivity from p-type to n-type with PbI₂-
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7 deficient and PbI₂ rich precursors both for MAPI and FAPI.³² Unfortunately, for the *d*-
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9 FAPI investigated in our work, any attempt to correlate composition to stoichiometry of
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11 precursors failed and the overall trend is found in the opposite direction as the films with x
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13 = 0.15 have been made using a stoichiometric ratio more PbI₂-deficient than the one used
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15 for $x \leq 0.13$ (Table S10). This suggests that other factors can influence the semiconductor
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17 doping type and level. Amongst others, it has been shown that thermal annealing can
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19 convert an initially p-type halide perovskite to n-type.³³
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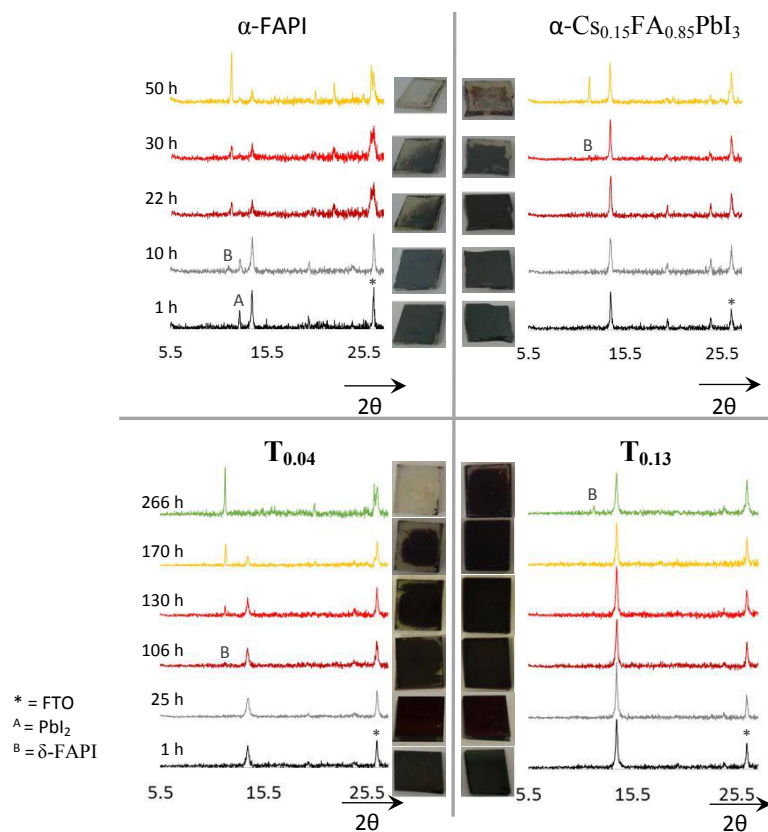


Figure 5. Stability test (ambient conditions: 25 °C, 75-90% humidity) of α -FAPbI₃, α -Cs_{0.15}FA_{0.85}PbI₃, **T**_{0.04}, **T**_{0.13} thin films. The XRD patterns and the pictures were realized in the 1-50 hours range and 1-266 hours range for α -FAPbI₃, α -Cs_{0.15}FA_{0.85}PbI₃ and **T**_{0.04}, **T**_{0.13}, respectively.

The α -phase air stability of **H**_{0.13}, **H**_{0.15}, **T**_{0.04} and **T**_{0.13} thin films has been compared to both α -FAPbI₃ and α -Cs_{0.15}FA_{0.85}PbI₃ samples. This mixed cation α -FAPbI₃ type perovskite has been selected as a reference material due to its higher α -phase stability and performances in solar cells.^{11,34,35} The corresponding thin films were prepared by spin-coating with a final annealing step at 125 °C for α -Cs_{0.15}FA_{0.85}PbI₃, **H**_{0.13}, **H**_{0.15}, **T**_{0.04}, **T**_{0.13}, and at 155°C for α -FAPbI₃ (more details in S.I. -X-). All these films were aged under ambient conditions (25

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3 °C, air with 75-90% humidity, ambient sunlight), without encapsulation and their aspect
4 and structural changes upon aging were followed (Figure 5 and Figures S26, S27). After 1
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6 hour, only the XRD pattern of α -FAPbI₃ thin film presented the typical peak of PbI₂ (12.8°
7 2 θ), a compound which is in fact generated during the annealing step at 155°C. After 10
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9 hours, the typical line of δ -FAPbI₃ at 11.7° 2 θ appeared in the XRD pattern of α -FAPbI₃, then
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11 the α -to- δ phase transformation was completed after around 50 hours of aging. α -
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13 Cs_{0.15}FA_{0.85}PbI₃ thin film owns a higher α -phase stability under ambient conditions than α -
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15 FAPbI₃ since the α -to- δ transformation starts after 30 hours and is completed between 50 and
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17 106 hours of aging (S.I. Figure S27). The **H**_{0.13} and **H**_{0.15} thin films exhibited a similar
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19 stability to the α -FAPbI₃ one (total transformation into δ -FAPbI₃ between 22 and 50 hours of
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21 aging, Figure S26). Importantly, the **T**_{0.04} and **T**_{0.13} thin films were significantly more
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23 stable. Indeed, the first sign of δ -phase formation occurred after 106 hours and 266 hours
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25 for **T**_{0.04} and **T**_{0.13}, respectively. This means that under ambient conditions, **T**_{0.13} thin films
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27 are approximately twenty times more stable than α -FAPbI₃ and ten times more stable than α -
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29 Cs_{0.15}FA_{0.85}PbI₃. This exceptional α -phase stability is presumably the consequence of the
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31 presence of the TEA⁺ cation inside the 3D perovskite network. Interestingly, taking into
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33 account that HEA⁺ and TEA⁺ cations own the same alkyl chain, and that their size and
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35 amounts of incorporation are similar, such a higher stability of **T**_{0.13} compared to **H**_{0.13}, is
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37 due to added benefit thanks to the thiol function as compared to the alcohol one. The thiol
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39 function is less hydrophilic and may make stronger interactions with the inorganic network,
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41 thus allowing a better stabilisation of the α -phase in air condition. This hypothesis of
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43 stronger interactions with the inorganic network is reinforced by the solid NMR data,
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3 which evidenced that TEA⁺ presents much less rotational mobility as compared to the two
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5 other organic cations considered in this work (FA⁺, HEA⁺).
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8 9 10 **CONCLUSION**

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12 In summary, we have shown that both HEA⁺ and TEA⁺ large cations (effective radius of
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14 3.44 Å and 4.14 Å, respectively) can be incorporated into a 3D [Pb_{1-x}I_{3-x}] α-FAPI type
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16 perovskite network, showing that it is possible to circumvent the geometrical Goldschmidt
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18 factor. The resulting phases *d*-α-FAPI-**H_x** and *d*-α-FAPI-**T_x** can be obtained by an easy
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20 precipitation method at room temperature, while the well-known α-FAPI parent phase can
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22 only be obtained above 150 °C. Incorporation of such larger size cations, particularly the
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24 thiol-cation TEA⁺, leads to thin films demonstrating exceptional α-phase stability under
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26 ambient conditions, surpassing the one of α-FAPI and α-Cs_{0.15}FA_{0.85}PbI₃ by more than an
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28 order of magnitude. The higher α-phase stability of *d*-α-FAPI-**T_x** materials compared to *d*-
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30 α-FAPI-**H_x** ones, points out the positive impact of the thiol function compared to alcohol
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32 function. This certainly originates from the less hydrophilic nature of –SH compared to –
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34 OH, and it may also indicate greater abilities of the thiol function to make quite strong
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36 interactions with the inorganic perovskite network, which leads to a slower motion of the
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38 TEA⁺ cations as evidenced by solid-state NMR. Besides, computational investigations
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40 correlated with experimental observations reveal the progressive opening of the direct band
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42 gap and increase of the effective masses when *x* increase from 0 to 0.13. For greater values
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44 of *x*, those trends remain but the evolution dramatically accelerates. Moreover, UV-visible,
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46 XPS and computational results suggest that *d*-α-FAPI compounds turn from p-type to n-
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48 type semiconductors for *x* values above 0.15. These observations prove that it is possible
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3 to accurately tune the electronic properties of this d - α -FAPbI₃ phases lead and iodide
4 deficient hybrid perovskite family (d -HP) by controlling x . Thus, d - α -FAPbI₃ materials
5 appears as serious MA⁺ and Br⁻-free candidates as an alternative to the widespread alloys
6 (Cs,MA,FA)Pb(I,Br)₃ for single junction but also tandem PSCs, which recently achieved
7 certified power conversion efficiencies of 28.0%.³ We believed that these results pave a
8 path to the discovery of new perovskite materials for energy applications thanks to the
9 greater versatility of defective sites.
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21 **ASSOCIATED CONTENT**

22 Supporting Information

23 The Supporting Information is available free of charge on the

24 ACS Publications website
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33 **AUTHOR INFORMATION**

34 Corresponding Authors

35 nicolas.mercier@univ-angers.fr ; claudine.katan@univ-rennes1.fr
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