

# How Photogenerated I<sub>2</sub> Induces I-Rich Phase Formation in Lead Mixed Halide Perovskites

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# How Photogenerated I<sub>2</sub> Induces I-Rich Phase Formation in Lead Mixed Halide Perovskites

Yang Zhou,\* Simone C. W. van Laar, Daniele Meggiolaro,\* Luca Gregori, Samuele Martani, Jia-Yong Heng, Kunal Datta, Jesús Jiménez-López, Feng Wang, E Laine Wong, Isabella Poli, Antonella Treglia, Daniele Cortecchia, Mirko Prato, Libor Kobera, Feng Gao, Ni Zhao, René A. J. Janssen, Filippo De Angelis, and Annamaria Petrozza\*

Bandgap tunability of lead mixed halide perovskites (LMHPs) is a crucial characteristic for versatile optoelectronic applications. Nevertheless, LMHPs show the formation of iodide-rich (I-rich) phase under illumination, which destabilizes the semiconductor bandgap and impedes their exploitation. Here, it is shown that how I<sub>2</sub>, photogenerated upon charge carrier trapping at iodine interstitials in LMHPs, can promote the formation of I-rich phase. I<sub>2</sub> can react with bromide (Br<sup>-</sup>) in the perovskite to form a trihalide ion I<sub>2</sub>Br<sup>-</sup> (I<sup>δ-</sup>-I<sup>δ+</sup>-Br<sup>δ-</sup>), whose negatively charged iodide (I<sup>δ-</sup>) can further exchange with another lattice Br<sup>-</sup> to form the I-rich phase. Importantly, it is observed that the effectiveness of the process is dependent on the overall stability of the crystalline perovskite structure. Therefore, the bandgap instability in LMHPs is governed by two factors, i.e., the density of native defects leading to I<sub>2</sub> production and the Br<sup>-</sup> binding strength within the crystalline unit. Eventually, this study provides rules for the design of chemical composition in LMHPs to reach their full potential for optoelectronic devices.

## 1. Introduction

Lead halide perovskites (LHPs, chemical formula APbX<sub>3</sub>, A = formamidinium (FA<sup>+</sup>), methylammonium (MA<sup>+</sup>), or Cs<sup>+</sup> and X = I<sup>-</sup>, Br<sup>-</sup>, or Cl<sup>-</sup>) have demonstrated their potential as a material platform for a new generation of optoelectronic technology. One superior feature of LHPs is their continuously tunable bandgap from near infrared to ultraviolet by substituting I<sup>-</sup> with Br<sup>-</sup> and Cl<sup>-</sup> at the X-site through simple solution processing.<sup>[1]</sup> This enables LHPs to provide top absorbers with matched bandgaps for tandem solar cells<sup>[2]</sup> and emissive layers for colorful light-emitting diodes (LEDs),<sup>[3]</sup> just to mention the most common applications. However, the bandgap tunability of LHPs cannot be practically attained

Y. Zhou, S. Martani, J. Jiménez-López, E. L. Wong, I. Poli, A. Treglia, D. Cortecchia, A. Petrozza  
Center for Nano Science and Technology@Polimi  
Istituto Italiano di Tecnologia  
via Rubattino 81, Milano 20134, Italy  
E-mail: yang.zhou@iit.it; annamaria.petrozza@iit.it  
S. C. W. van Laar, K. Datta, R. A. J. Janssen  
Molecular Materials and Nanosystems  
Institute for Complex Molecular Systems  
Eindhoven University of Technology  
P.O. Box 513, Eindhoven 5600 MB, The Netherlands

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202305567>

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D. Meggiolaro, L. Gregori, F. De Angelis  
Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO)  
Istituto CNR di Scienze e Tecnologie Chimiche “Giulio Natta”  
(CNR-SCITEC)  
Via Elce di Sotto 8, Perugia 06123, Italy  
E-mail: daniele.meggiolaro@cnr.it  
L. Gregori, F. De Angelis  
Department of Chemistry  
Biology and Biotechnology  
University of Perugia and INSTM  
Via Elce di Sotto 8, Perugia 06123, Italy  
J.-Y. Heng, N. Zhao  
Electronic Engineering Department  
The Chinese University of Hong Kong  
Shatin, NT 999077, Hong Kong  
F. Wang, F. Gao  
Department of Physics  
Chemistry and Biology  
Linköping University  
Linköping SE-581 83, Sweden

because of the I-rich phase formation under illumination.<sup>[4]</sup> The I-rich phase acts as charge carrier funneling center, reducing the performance of solar cells<sup>[5]</sup> and redshifting the emission in LEDs.<sup>[6]</sup> To reach the full potential of LHPs in optoelectronic applications, it is indispensable that the fundamentals behind the photoinstability are comprehensively understood.

Since the first report,<sup>[4]</sup> multiple models have been proposed to explain the processes behind light-induced I-rich phase formation, whereas no one to date fully rationalizes the diverse observations upon such phenomenon and its origin is still under debate. In mixed-halide perovskites APb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, it has been shown that the formed I-rich phase has a specific Br-fraction  $x$  of  $\approx 0.2$ <sup>[4]</sup> under illumination. This is explained by thermodynamically favored phase segregation following a phase diagram and possibly roots in the escalated strain due to preferential anion lattice spacings<sup>[7]</sup> or electron-phonon coupling<sup>[8]</sup> under illumination. The phase diagram was further reconstructed by coupling the presence of photo-generated carrier with thermodynamical modeling.<sup>[9]</sup> The strain-based models are supported by the suppressed I-rich phase formation by incorporating Cs<sup>+</sup> at A-site, which is suggested to weaken lattice polaron formation<sup>[10]</sup> or static microstrain.<sup>[11]</sup> However, these models indicate a temperature-dependent Br-fraction in the formed I-rich phase, while a recent study shows  $x$  having little to no temperature dependence which suggests a thermodynamic bandgap-based model.<sup>[10a,12]</sup>

The role of defect activity in light-induced I-rich phase formation is gaining more and more consensus. Multiple reports suggest that local electrical field created by photocarrier trapping<sup>[5a,13]</sup> or strong photocarrier gradient<sup>[14]</sup> could cause unbalanced halide migration and I-rich phase formation under illumination. Halide vacancies are likely to provide the primary halide migration pathway.<sup>[13d,15]</sup> Pure-iodide lead perovskite has shown enhanced ionic conductivity under illumination, which is attributed to the increased iodide vacancies formed through I<sup>-</sup> oxidation by photocarriers.<sup>[16]</sup> Furthermore, it has been shown that in mixed I-Br perovskites, photoexcitation boosts the transportation of I<sup>-</sup> rather than Br<sup>-</sup>, since I<sup>-</sup> has lower oxidation potential and its vacancies are mainly generated.<sup>[17]</sup>

It is now well accepted that I<sub>2</sub> is one of the main products upon photocarrier trapping in tri-iodide lead perovskite<sup>[18]</sup> and contributes to its photo-degradation<sup>[19]</sup> Recently, we demonstrated that the formation of I-rich phase in mixed I-Br perovskites is closely correlated with the carrier trapping at interstitial iodide defects and the formation of I<sub>2</sub>, thus indicating that photo-degradation in tri-iodide and bandgap instability in mixed I-Br perovskites may have the same root.<sup>[20]</sup> Here, we show how the

photogenerated I<sub>2</sub> induces the I-rich phase formation in mixed I-Br perovskites. To rationalize the mechanism, we exposed mixed I-Br and pure-Br perovskites to I<sub>2</sub> vapor in the dark; both materials show the formation of I-rich phase after I<sub>2</sub> treatment. Through combined optical spectroscopies, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) analyses and computational studies, we propose that I<sub>2</sub> react with Br<sup>-</sup> to form the intermediate triple halide ion I<sub>2</sub>Br<sup>-</sup> (I<sup>δ-</sup>-I<sup>δ+</sup>-Br<sup>δ-</sup>), which leads to I<sup>-</sup> formation through a series of chemical reactions, and thus increases the local I<sup>-</sup> to Br<sup>-</sup> ratio in the perovskite. Our model rationalizes how the prominence of I<sub>2</sub> formation under illumination, and binding strength of Br<sup>-</sup> with respect to its ability to react with I<sub>2</sub> regulate the formation of I<sub>2</sub>Br<sup>-</sup> and I-rich phase, providing the guidance for achieving photostable mixed I-Br perovskites and devices.

## 2. Results and Discussion

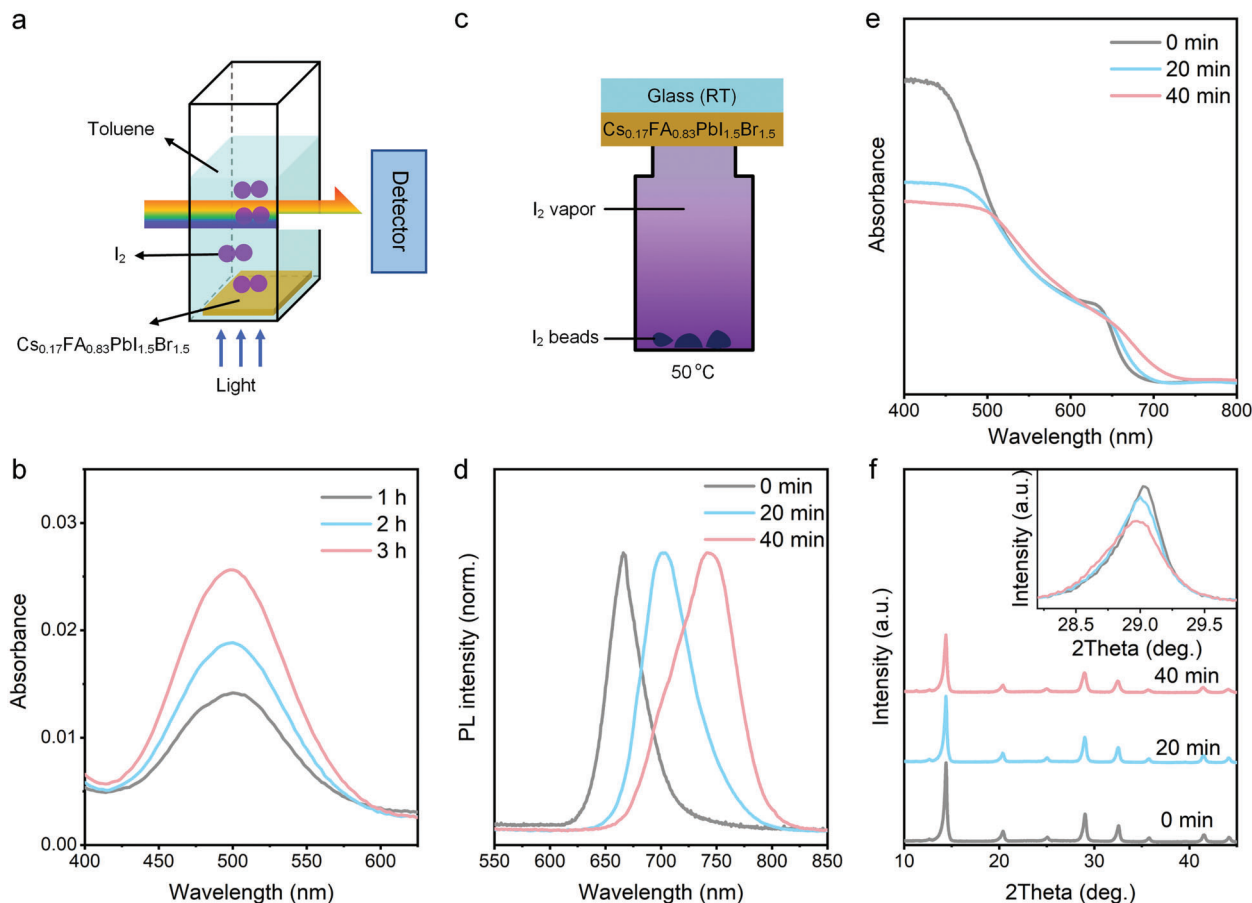
### 2.1. Impact of I<sub>2</sub> Exposure on Lead Mixed I-Br and Pure-Br Perovskites

Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite with a bandgap of 1.85 eV was first used as a model material for our study.<sup>[2,21]</sup> The thin film was prepared by an anti-solvent method<sup>[22]</sup> (details provided in Experimental Section). We first checked the photo-induced I<sub>2</sub> formation by immersing the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> thin film in anhydrous toluene under a white LED with intensity calibrated to 1 sun at 30 °C. The evolution of I<sub>2</sub> formation is monitored by measuring the ultraviolet-visible (UV-Vis) absorption of the anhydrous toluene in contact with the perovskite film.<sup>[19b]</sup> **Figure 1** shows the schematic of the I<sub>2</sub> formation experiment. As shown in Figure 1b, the I<sub>2</sub> absorption signal is detected in toluene after light soaking and becomes more intense with longer soaking time (up to 3 h), which indicates the I<sub>2</sub> formation in the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite. A recent study from Martani et al. shows a correlation between I-rich phase formation under illumination and I<sub>2</sub> generation through charge carriers trapping at iodide interstitials.<sup>[20]</sup> The latter is accompanied by the increase of iodide vacancies.<sup>[13d,15,16]</sup> Thus, to investigate the sole effect of I<sub>2</sub> on altering optical and structural properties without increasing iodide vacancies<sup>[13d,15,16]</sup> in the mixed I-Br perovskite, we exposed the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite to I<sub>2</sub> vapor in the dark. Note that I<sub>2</sub> treatment was performed in a N<sub>2</sub>-filled glovebox. Figure 1c shows a schematic of the experiment, during which the I<sub>2</sub> beads were heated at 50 °C as the source of I<sub>2</sub> vapor and the sample was kept at room temperature (RT). The pristine film shows a photoluminescence (PL) emission at 670 nm. Following I<sub>2</sub> vapor exposure, the PL peak broadens and redshifts to 702 and 744 nm after 20 and 40 min, respectively (Figure 1d). Meanwhile, the onset of UV-Vis absorption spectrum redshifts and flattens upon I<sub>2</sub> exposure (Figure 1e). These results indicate that I<sub>2</sub> treatment induces the formation of I-rich phase with high energetic disorder. The X-ray diffraction pattern (XRD) of the pristine perovskite shows two main peaks at 14.40° and 29.02° which correspond to the (100) and (200) planes of a cubic lattice, respectively (Figure 1f).<sup>[1b]</sup> Over 40 min of I<sub>2</sub> exposure, the (200) diffraction peak shifts to lower angle and widens, but with a negligible growth at the high-angle tail (inset of Figure 1f). This demonstrates the overall expansion of the perovskite lattice with increased structural disorder.

M. Prato  
Materials Characterization Facility  
Istituto Italiano di Tecnologia  
Via Morego, Genova 16163, Italy

L. Kobera  
Institute of Macromolecular Chemistry  
Czech Academy of Sciences  
Heyrovsky Sq. 2, Prague 6 162 06, Czech Republic

F. De Angelis  
SKKU Institute of Energy Science and Technology (SIEST)  
Sungkyunkwan University  
Suwon 440-746, South Korea



**Figure 1.** a) Schematic of monitoring  $I_2$  formation in  $Cs_{0.17}FA_{0.83}PbI_{1.5}Br_{1.5}$  perovskite under illumination (a white light LED with an intensity of  $100 \text{ mW cm}^{-2}$ ). The thin film sample is placed in toluene and the  $I_2$  signal in toluene is measured by absorption spectroscopy. b) Evolution of  $I_2$  formation in  $Cs_{0.17}FA_{0.83}PbI_{1.5}Br_{1.5}$  thin film under illumination over 3 h. c) Schematic of  $I_2$  vapor exposure to the  $Cs_{0.17}FA_{0.83}PbI_{1.5}Br_{1.5}$  thin film in the dark and in the  $N_2$ -filled glovebox. The sample is kept at room temperature (RT). d) PL spectra, e) UV-Vis absorption spectra and f) XRD patterns of  $Cs_{0.17}FA_{0.83}PbI_{1.5}Br_{1.5}$  perovskite upon  $I_2$ -vapor exposure in the dark over 40 min.

Combined with PL and absorption results (Figures 1d,e), the lattice expansion observed in the perovskite exposed to  $I_2$  can be attributed to the overall enrichment of  $I^-$  in the lattice. Since the  $I^-$  ratio in the perovskite lattice directly relates to the XRD peak position,<sup>[1b]</sup> we can estimate that the average  $I^-$  ratio  $\gamma$  ( $\gamma = 1-x$ ,  $x$  is  $Br^-$  ratio) is increased by 0.008 and 0.018 upon  $I_2$  vapor exposure for 20 and 40 min, respectively (Figure S1 and Table S1, Supporting Information). The detail of the estimation is given on page 4 in Supporting Information. The enrichment of  $I^-$  in the perovskite lattice requires extra  $I^-$  and implies  $I_2$  being the  $I^-$  source.

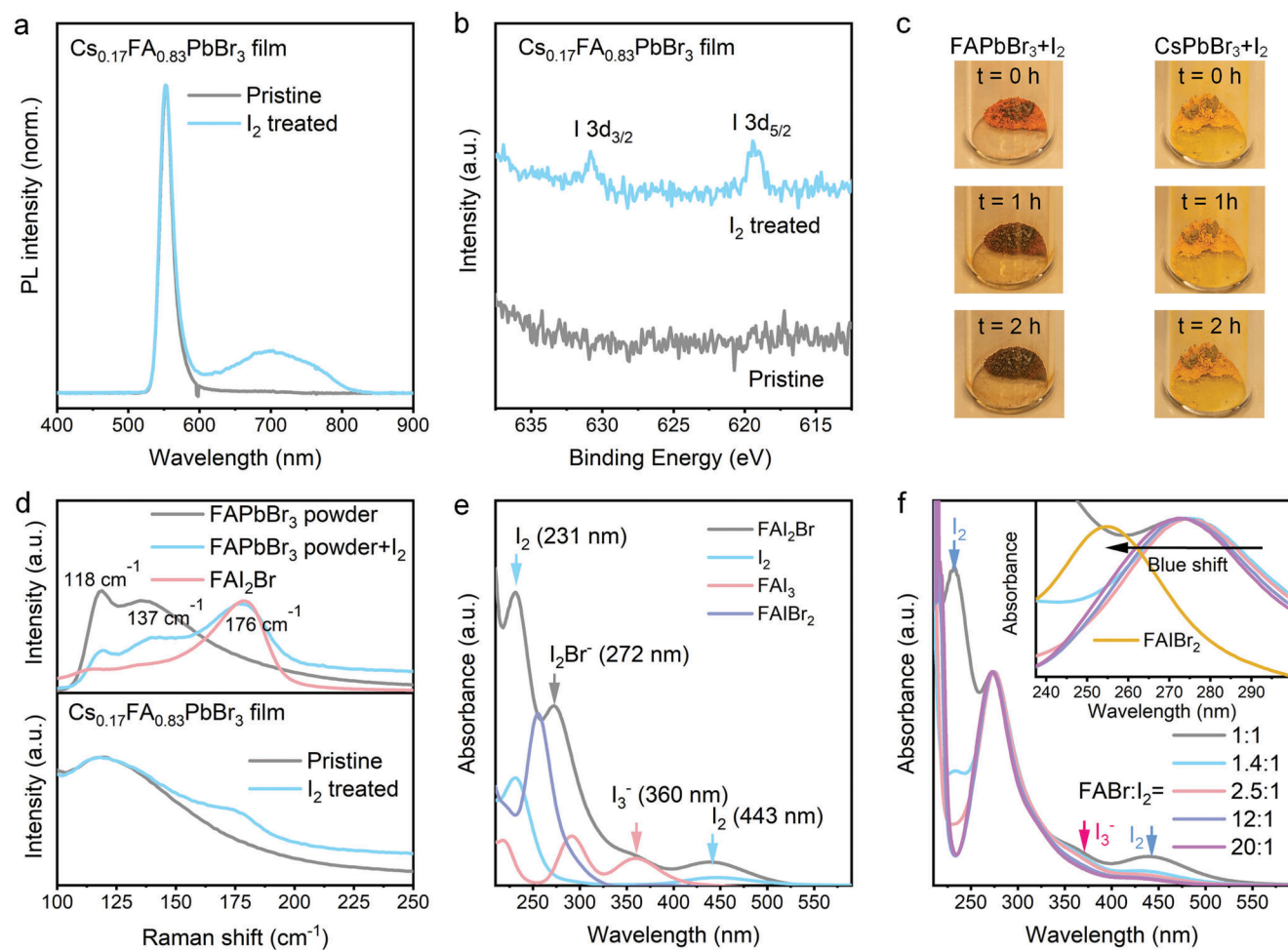
To confirm that the extra  $I^-$  enriching the  $Cs_{0.17}FA_{0.83}PbI_{1.5}Br_{1.5}$  perovskite lattice is produced by  $I_2$ , we further tested  $I_2$  exposure on the pure-Br perovskite of  $Cs_{0.17}FA_{0.83}PbBr_3$ . The pristine sample shows a PL emission at 550 nm (Figure 2a). After exposure to  $I_2$  vapor for 20 min, we observe the emergence of a broad band peaking at  $\approx 705 \text{ nm}$  (Figure 2a). This implies the formation of the I-rich phase with a broad  $I^-$  to  $Br^-$  distribution. X-ray photoelectron spectroscopy (XPS) was further conducted for elemental analysis. The spectra of  $I 3d$  are shown in Figure 2b and those of the other elements in the perovskite are given in Figure S2 (Supporting Information).

The pristine sample does not show any signal from the iodine species according to the XPS spectrum (Figure 2b), while after  $I_2$  treatment a weak XPS peak of  $I 3d_{5/2}$  emerges at a binding energy of  $(619.0 \pm 0.2) \text{ eV}$  (Table S2, Supporting Information). This should be assigned to  $I^-$  but not  $I_2$ , since  $I 3d_{5/2}$  of  $I_2$  is at  $\approx 620 \text{ eV}$ .<sup>[23]</sup> This confirms that  $I_2$  can be converted to  $I^-$  when in contact with the perovskite, which can further incorporate into the lattice. The concentration of  $I^-$  in the  $I_2$ -treated  $Cs_{0.17}FA_{0.83}PbBr_3$  perovskite is quantified based on the XPS spectrum with a value of 0.3 at% (Table S3, Supporting Information). Though this indicates that the formed I-rich phase in the  $Cs_{0.17}FA_{0.83}PbBr_3$  perovskite after  $I_2$  exposure may be in a small quantity, it is still able to act as charge funneling center and redshift the PL emission.<sup>[5b]</sup>

## 2.2. Mechanism behind $I_2$ Induced I-Rich Phase Formation

We further investigated the possible process of converting  $I_2$  to  $I^-$  when  $I_2$  is in contact with Br-containing perovskite. We exclude the possibility of  $I^-$  formation through the oxidation of  $Br^-$  by  $I_2$ , because of the much higher oxidation potential of  $Br^-$  (1.07 V) than that of  $I^-$  (0.53 V) (see the analysis in Supporting





**Figure 2.** a) PL and b) XPS spectra of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  before and after 20 min  $\text{I}_2$  vapor exposure. c) Photo images of the  $\text{FAPbBr}_3\text{-I}_2$  and  $\text{CsPbBr}_3\text{-I}_2$  mixtures over 2 h. d) Raman spectra of  $\text{FAPbBr}_3$  powder and  $\text{FAPbBr}_3\text{-I}_2$  mixture after 2 h mixing. The Raman spectrum of  $\text{FAI}_2\text{Br}$  is given for reference. e) Raman spectra of  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  perovskite thin films before and after  $\text{I}_2$  exposure. f) UV-Vis absorption spectra of  $\text{FAI}_2\text{Br}$ ,  $\text{FAI}_3$ ,  $\text{FAI}_2\text{Br}_2$ , and  $\text{I}_2$  dissolved in ethanol.  $\text{FAI}_2\text{Br}$ ,  $\text{FAI}_3$  and  $\text{FAI}_2\text{Br}_2$  are prepared by mixing  $\text{FABr}$  with  $\text{I}_2$ ,  $\text{FAI}$  with  $\text{I}_2$ , and  $\text{FABr}$  with  $\text{IBr}$  in a mole ratio of 1 : 1, respectively. g) UV-Vis absorption spectra of  $\text{FABr-I}_2$  mixtures in ethanol by varying  $\text{FABr}$  to  $\text{I}_2$  mole ratio from 1:1 to 20:1. The inset shows the blueshift of the absorption feature of  $\text{I}_2\text{Br}^-$  by increasing the  $\text{FABr}$  to  $\text{I}_2$  ratio.

Information).  $\text{I}_2$  is a well-known electron acceptor in the presence of ionic halide electron donors like  $\text{Br}^-$ , forming a wide variety of triple halide species including  $\text{I}_2\text{Br}^-$  [24] during which the neutral iodine ( $\text{I}^0$ ) becomes partially positively and negatively charged in  $\text{I}_2\text{Br}^-$  ( $\text{I}^{\delta-}\text{-I}^{\delta+}\text{-Br}^{\delta-}$ ) [25]:



The charge density of the cation bonded with halide ions affects their ability of donating electrons and thus the ability to form triple halide ions with  $\text{I}_2$ . [26] We first checked the feasibility of  $\text{I}_2\text{Br}^-$  formation in a pure FA, a pure Cs and a mixed Cs-FA environment by mixing  $\text{FABr}$ ,  $\text{CsBr}$ , and  $\text{I}_2$  in a molar ratio of (1: 0: 1), (0: 1: 1) and (0.17: 0.83: 1) at a temperature of 25 °C, respectively. It is shown that in the two environments containing FA, the mixtures of bromide salts and  $\text{I}_2$  show prominent reaction to form a dark red compound, while no visible reaction can be observed in the pure-Cs environment (Figure S3a, Supporting In-

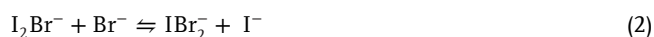
formation). Polyhalides typically yield intense Raman signals due to the large polarizability of their electron-rich structures [27]; thus, we exploited this technique to probe their formation. The Raman spectrum of the compound formed in the FA-containing environments matches that of the  $\text{I}_2\text{Br}^-$  ion (Figures S3b,c, Supporting Information), [27] suggesting its formation in this scenario. With the presence of  $\text{Cs}^+$ , the formation of the  $\text{I}_2\text{Br}^-$  ion is suppressed and is possibly due to higher charge density (smaller radius) of  $\text{Cs}^+$  than  $\text{FA}^+$  (Figure S3a, Supporting Information), which binds  $\text{Br}^-$  more tightly and increases the negative charge localization near the cation, and thus weakens the capability of  $\text{Br}^-$  to polarize  $\text{I}_2$  to form the triple halide ion. [26]

We further synthesized  $\text{FAPbBr}_3$  and  $\text{CsPbBr}_3$  powders and mixed them separately with  $\text{I}_2$  in a molar ratio of 1:1 to check their feasibility of reacting with  $\text{I}_2$ . Over a period of 2 h, the  $\text{FAPbBr}_3\text{-I}_2$  mixture shows prominent change in color, while that of  $\text{CsPbBr}_3\text{-I}_2$  mixture shows no visible change (Figure 2c). Raman measurement was also conducted on the  $\text{FAPbBr}_3$  powder

and FAPbBr<sub>3</sub>-I<sub>2</sub> mixture (after 2 h mixing), to elucidate the reaction happening behind the color change. As shown in Figure 2d, the FAPbBr<sub>3</sub> powder shows two peaks at 118 and 137 cm<sup>-1</sup>, which are assigned to the coupled modes between the organic cation motion influenced by the inorganic octahedral (Figure 2d).<sup>[28]</sup> After mixing with I<sub>2</sub>, one additional vibration mode centered at 176 cm<sup>-1</sup> appears in the spectrum, which indicates the formation of I<sub>2</sub>Br<sup>-</sup><sup>[27]</sup> (The Raman spectra of FAI<sub>2</sub>Br is given as a reference, Figure 2d). In the CsPbBr<sub>3</sub>-I<sub>2</sub> mixture no I<sub>2</sub>Br<sup>-</sup> can be detected by Raman spectroscopy (Figure S4, Supporting Information), indicating the suppression of the triple halide formation compared with the FA counterpart. The different reactivity of FAPbBr<sub>3</sub> and CsPbBr<sub>3</sub> with I<sub>2</sub> to form I<sub>2</sub>Br<sup>-</sup> support the role of the A-site cation in the process.

Based on these results, we further elucidate the processes that are occurring when Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> thin film is exposed to I<sub>2</sub> vapor. Raman spectra of the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> thin film before and after I<sub>2</sub> vapor exposure were measured. Compared with FAPbBr<sub>3</sub>, the two peaks of 118 and 137 cm<sup>-1</sup> merges into a broad peak in the spectrum of pristine Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> (Figure 2e), which is possibly due to the incorporation of Cs at A-site affecting the coupled modes between the organic cation motion. In addition, the Raman feature of I<sub>2</sub>Br<sup>-</sup> at 176 cm<sup>-1</sup> arises after I<sub>2</sub> vapor exposure, which indicates the formation of I<sub>2</sub>Br<sup>-</sup> (Figure 2e).

It has been reported that I<sub>2</sub>Br<sup>-</sup> can further produce IBr<sub>2</sub><sup>-</sup> (Br<sup>δ-</sup>-I<sup>δ+</sup>-Br<sup>δ-</sup>)<sup>[25]</sup> and I<sup>-</sup> by reacting with another Br<sup>-</sup><sup>[29]</sup>:



To confirm this, we dissolved FAI<sub>2</sub>Br in ethanol, and measured the absorption by UV-Vis spectroscopy. The absorption spectra of I<sub>2</sub>, FAI<sub>3</sub> and FAIBr<sub>2</sub> dissolved in ethanol were also measured as references. FAI<sub>3</sub> and FAIBr<sub>2</sub> were prepared by mixing FAI with I<sub>2</sub> and FAbBr with IBr in a molar ratio of 1:1, respectively. The absorption spectrum of FAI<sub>2</sub>Br shows peaks at 231, 272, 360, and 443 nm (Figure 2f). The peak at 272 nm indicates the formation I<sub>2</sub>Br<sup>-</sup> (Figure 2f).<sup>[29]</sup> Peaks at 231 and 443 nm belongs to I<sub>2</sub> (Figure 2f), and indicates the conversion of Br<sup>-</sup> and I<sub>2</sub> to I<sub>2</sub>Br<sup>-</sup> is incomplete. In addition, the peak at 360 nm is assigned to I<sub>3</sub><sup>-</sup> (Figure 2f), which indicates the existence of I<sup>-</sup> ions in the solution and they can combine with residual I<sub>2</sub> to form I<sub>3</sub><sup>-</sup>:



Therefore, this confirms that I<sup>-</sup> can be produced through Rxn. 2. Through the available thermodynamic data, the reaction constant *K* of Rxn. 2 at 25 °C can be further obtained<sup>[29,30]</sup>:

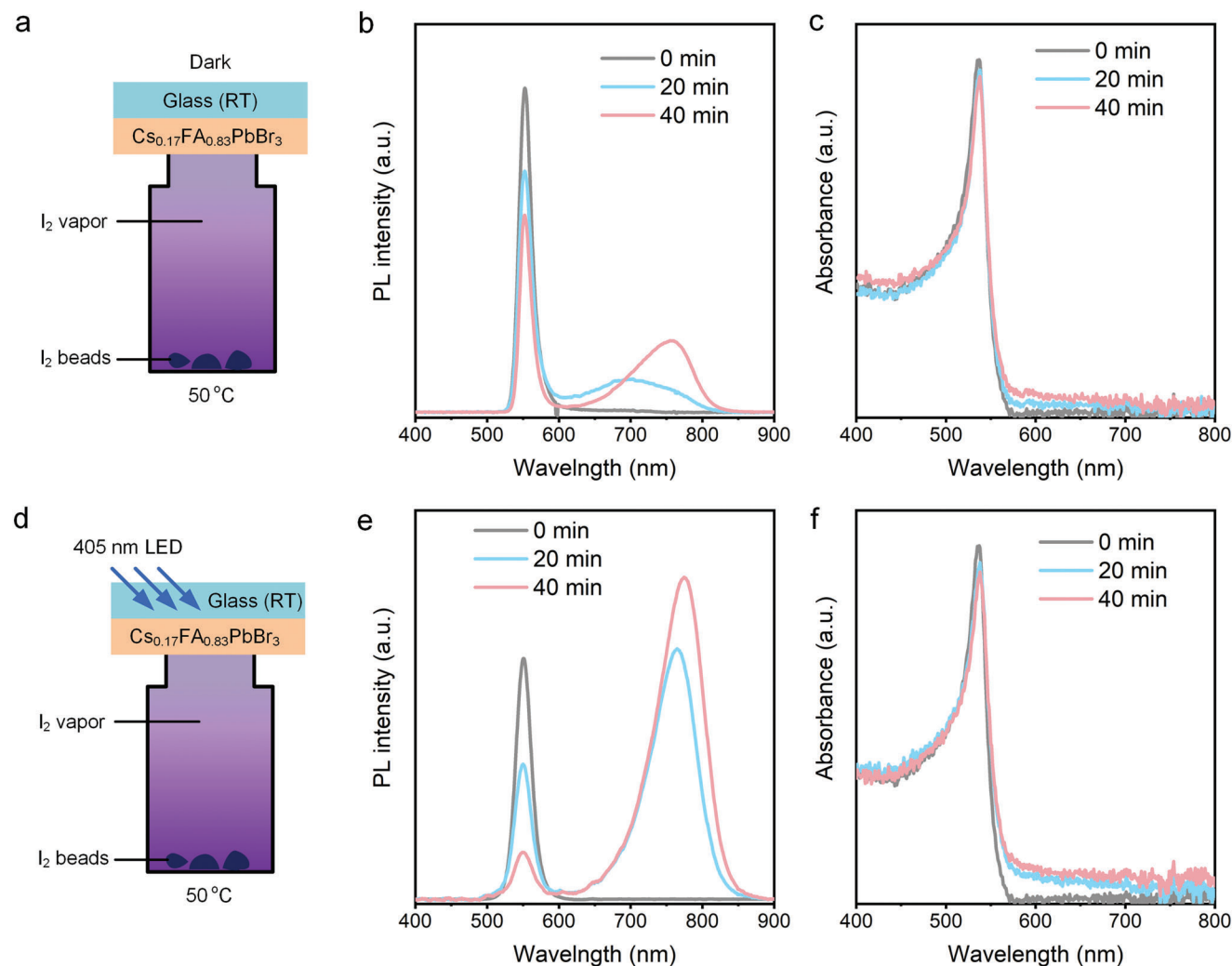
$$K = \frac{(\text{IBr}_2^-)(\text{I}^-)}{(\text{I}_2\text{Br}^-)(\text{Br}^-)} = 1.4 \times 10^{-4} \quad (4)$$

As such, the concentration of formed IBr<sub>2</sub><sup>-</sup> may be much lower than that of I<sub>2</sub>Br<sup>-</sup>, whose absorption feature (at 255 nm shown in Figure 2f) may be buried under that of I<sub>2</sub>Br<sup>-</sup>. Extra FAbBr is further introduced in the solution of FAI<sub>2</sub>Br to verify the Rxns. 1–3. By increasing FAbBr to I<sub>2</sub> ratio from 1:1 to 20:1, the absorption feature of I<sub>2</sub>Br<sup>-</sup> shows a blueshift (inset of Figure 2g) toward that of IBr<sub>2</sub><sup>-</sup> at 255 nm, which indicates the increase of IBr<sub>2</sub><sup>-</sup> concentration and confirms the occurrence of Rxn. 2.<sup>[29]</sup>

Meanwhile, the signals of both I<sub>2</sub> and I<sub>3</sub><sup>-</sup> diminishes upon increasing of Br<sup>-</sup> (Figure 2g), confirming the consumption of I<sub>2</sub> to form more I<sub>2</sub>Br<sup>-</sup> (Rxn. 1) and also the suppression of forming I<sub>3</sub><sup>-</sup> (Rxn. 3). By far, the processes of how I<sub>2</sub> can convert to I<sup>-</sup> when exposed to Br-containing perovskite is explained.

### 2.3. Comparison of I<sub>2</sub> Induced I-Rich Phase Formation in the Dark and under Illumination

So far, we have only investigated the effects of I<sub>2</sub> exposure in the dark. The notorious I-rich phase formation happens in lead mixed I-Br perovskites under illumination. Illumination may not only induce I<sub>2</sub> formation (Figures 1a,b), but also alters the kinetics of the reactions between I<sub>2</sub> and the perovskite. The pure-Br (Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub>) rather than the mixed I-Br (Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub>) perovskite is used for the investigation of I<sub>2</sub> exposure under illumination, to avoid the influence of I<sub>2</sub> inherently formed in the perovskite. The PL and UV-Vis absorption spectra of the perovskite after I<sub>2</sub> exposure in the dark and under illumination were both collected for comparison and are shown in Figure 3. In the dark, an additional emission peaking at 705 nm shows up in the PL of Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> after 20 min of I<sub>2</sub> exposure, which further redshifts to 758 nm after 40 min exposure (Figure 3b). The absorption of the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> perovskite upon I<sub>2</sub> exposure increases slightly in the longer wavelength range and mainly below 700 nm (Figure 3c). Meanwhile, though the I-rich phase with absorption edge at ≈758 nm cannot be detected by UV-Vis absorption spectroscopy (Figure 3c), the charge carriers can still be funneled to this phase and recombine radiatively, which indicates the I-rich phase with lowest bandgap can redshift the PL strongly even with a very minor quantity. Under illumination with a 405 nm diode laser with an intensity of 50 mW cm<sup>-2</sup> (Figure 3d), the PL emission of I-rich phase shows more significant redshift than in the dark, to 763 and 774 nm after 20 and 40 min of I<sub>2</sub> exposure, respectively (Figure 3e). By monitoring the PL behavior within the first 90 s under illumination and I<sub>2</sub> exposure, we find that the PL maxima of the I-rich phase reaches 690 nm within 30 s, and then redshift rapidly to 756 nm within 90 s (Figure S5, Supporting Information). Therefore, PL redshift of the I-rich phase is identical in trend but much more rapid under illumination when compared with the PL shift in the dark upon I<sub>2</sub> exposure (Figure 3b,e; Figure S5, Supporting Information). Meanwhile, the absorption increases more significantly at the longer wavelength upon I<sub>2</sub> exposure under illumination than in the dark, and the increase in the 700 to 800 nm range is clearly observed (Figure 3f). This indicates the faster formation rate of I-rich phase and thus the faster redshift of its PL in the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> perovskite under illumination than in the dark upon I<sub>2</sub> exposure (Figures 3b,e; and Figure S5, Supporting Information). We have shown that the Br<sup>-</sup> binding strength in the chemical environment defines the formation rate of I<sup>-</sup> (through Rxns. 1–2) and thus I-rich phase (Figure 2; Figure S3, Supporting Information) upon I<sub>2</sub> exposure. It is expected that the bond of Br<sup>-</sup> to the lattice is weakened when the perovskite is under photo-excitation, as the electron is promoted from the valence band, contributed by the mixing of the halide-lead orbitals, to the conduction band, contributed only



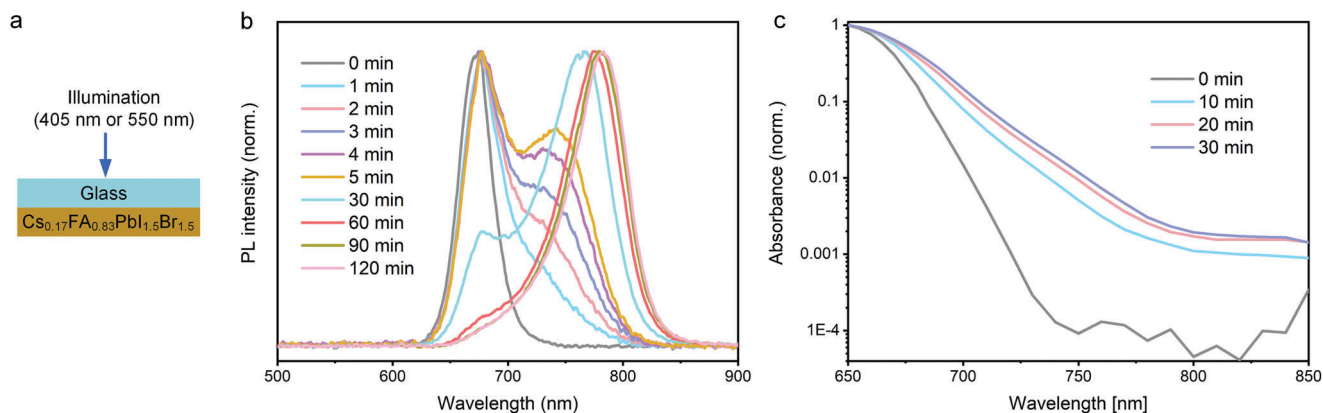
**Figure 3.** a) Schematic of  $\text{I}_2$  exposure on the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  perovskite thin film in the dark. Evolution of b) PL and c) UV-Vis absorption of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  perovskite thin film upon  $\text{I}_2$  exposure in the dark. d) Schematic of  $\text{I}_2$  exposure on the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  perovskite thin film under illumination. Evolution of e) PL and f) UV-Vis absorption of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$  perovskite thin film upon  $\text{I}_2$  exposure under illumination.

by the lead orbitals.<sup>[31]</sup> The reduced binding strength of  $\text{Br}^-$  may also increase concentration of  $\text{Br}^-$  interstitials due to the reduced energy barrier of forming the Frenkel pair. Therefore, halide exchange through Rxn. 2 is increased, either by reacting with  $\text{Br}^-$  from the lattice (with weakened binding strength) or by reacting with interstitial  $\text{Br}^-$  (free of binding) at a higher concentration. Therefore, it is expected to have an overall higher  $\text{I}^-$  concentration in the perovskite lattice upon  $\text{I}_2$  exposure under illumination than in the dark as reflected by PL and UV-Vis absorption results (Figure 3).

#### 2.4. Mechanism behind Photo-Induced I-Rich Phase Formation in Mixed I-Br Perovskites

Based on the investigation of the effects of  $\text{I}_2$  exposure by using the mixed I-Br and pure-Br perovskites, we elucidate the possible processes behind the widely known photo-induced I-rich phase formation in mixed I-Br perovskites.<sup>[4]</sup> It has been reported

that PL emission at a specific wavelength is commonly observed when the mixed I-Br perovskite is under illumination, which corresponds to a perovskite with a Br-fraction  $x$  of  $\approx 0.2$ .<sup>[1b,4]</sup> Multiple strain-based models suggest that this is because of a halide phase segregation process complying with a phase diagram.<sup>[7a,8]</sup> However, Suchan and co-workers revealed recently that the formed I-rich phase does not show a specific Br-fraction through combined PL and XRD analysis.<sup>[32]</sup> Here, we monitored the PL evolution of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  thin film under continuous illumination of a 405 nm diode laser with an intensity  $\approx 50 \text{ mW cm}^{-2}$  over 120 min. At the initial stage of the PL evolution, it seems that the newly formed PL emission is at a specific wavelength ( $\approx 743 \text{ nm}$ , Figure 4b) within a short period of 5 min. However, the newly emerged PL emission redshifts all the way to 780 nm (Figure 4b) which is close to that of  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$  pure iodide perovskite at 786 nm (Figure S6, Supporting Information). This suggests an I-enrichment, other than a phase segregation process, is happening when the mixed halide perovskite is under continuous illumination. This is further confirmed by



**Figure 4.** a) Schematic of inducing the I-rich phase formation in the perovskite. For PL and PDS measurements, the light sources used are a 405 nm ( $50 \text{ mW cm}^{-2}$ ) and 550 nm ( $100 \text{ mW cm}^{-2}$ ) diode lasers, respectively. b) PL evolution of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  perovskite thin film under illumination over 120 min. c) Evolution of PDS spectrum of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  perovskite thin film under illumination over 30 min.

photothermal deflection spectroscopy (PDS), that during the illumination of the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  perovskite over 30 min with a 550 nm diode laser ( $100 \text{ mW cm}^{-2}$ ), the I-rich phase with the lowest bandgap always has the lowest quantity (Figure 4c), which does not support the preferential formation of an I-rich phase with a specific Br-fraction. A recent study from Ridzonova and co-workers demonstrated identical behaviors of PL and formation of I-rich phase in the mixed I-Br perovskite.<sup>[33]</sup>

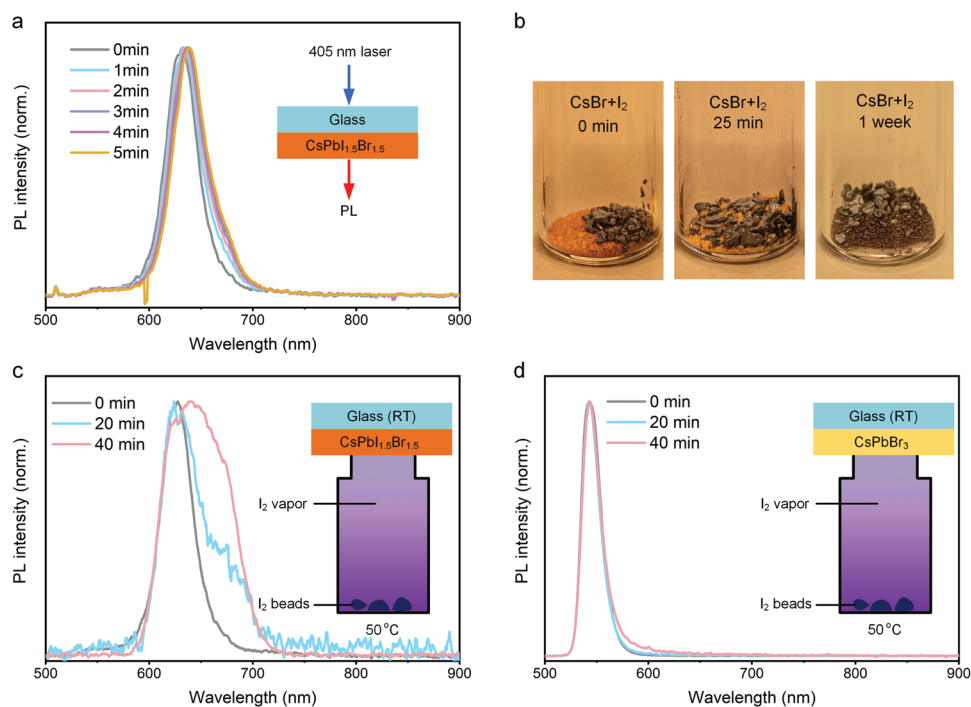
Based on the results shown above, we propose the following mechanism behind the photo-induced I-rich phase formation. Under illumination,  $\text{I}_2$  is first formed in the mixed I-Br perovskite (Figures 1a,b), which is then expelled to the grain boundary due to the relief of the lattice strain.<sup>[19a,34]</sup> Considering the grain boundary is a relatively closed space, we estimated that  $\text{I}_2$  can reach its saturated vapor pressure there within tens of seconds, based on the  $\text{I}_2$  formation rate derived from Figure 1b and the volume of the grain boundary estimated from SEM image of the perovskite (Figure S7, see Supporting Information for the detail of the estimation).  $\text{I}_2$  can then interact with  $\text{Br}^-$  at the grain surface to produce  $\text{I}^-$  following Rxns. 1 and 2, which further enters the perovskite lattice and causes the formation of I-rich phase. The formation of I-rich phase has indeed been observed to initiate from the grain boundaries.<sup>[8,13c]</sup> As this is an I-enrichment process, the I-rich phase with higher I-concentration (lower bandgap) has slower rate to be formed, which causes a distribution of I-rich phase quantity from high to low following the decrease of bandgap (Figure 4c). However, the PL emission of I-rich phase is dominated by the one with the lowest bandgap due to the strong charge funneling, and this emission will redshift continuously toward that of the pure iodide perovskite upon illumination (Figure 4b), as the I-content in the I-rich phase with the lowest bandgap will be enriched toward that of pure iodide perovskite.

Importantly, please note that photo-induced I-rich phase formation was initially reported as reversible in mixed I-Br perovskites.<sup>[4]</sup> Also after being transferred to a  $\text{N}_2$  ( $\text{I}_2$ -free) environment, the PL of the  $\text{I}_2$ -treated  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  thin film slowly (over several hours Figure S15a, Supporting Information) goes back to the original peak at higher energy. This is possible due to the reversal of Rxns. 1 and 2 once  $\text{I}_2$  supply stops. For the

photoaged mixed I-Br perovskites being stored in the dark, the photogeneration of  $\text{I}_2$  stops which may also cause the reversal of Rxns. 1 and 2 and the release of  $\text{I}_2$  to the grain boundary due to the decomposition of  $\text{I}_2\text{Br}^-$ . Then  $\text{I}_2$  may react with  $\text{Pb}^0$  (another byproduct of photodecomposition) to form perovskite again which could cause the reversal of halide segregation.<sup>[18b]</sup> However, Knight and co-workers found that reversibility highly depends on the photo-aging environment and history of the mixed I-Br perovskite.<sup>[13e]</sup> Specifically, halide segregation is mostly reversible when the film is encapsulated with a PMMA layer, while it is apparently not reversible in vacuum.<sup>[13e]</sup> Moreover, the reversibility is reduced with more cycles of light illumination.<sup>[13e]</sup> These observations agree with a reversibility correlated with the probability of  $\text{I}_2$  escaping the perovskite. The suppression of photo-induced halide segregation at elevated temperature up to  $70^\circ\text{C}$  has been reported.<sup>[35]</sup> We found that the recovery of PL of the  $\text{I}_2$ -treated  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  thin film in a  $\text{N}_2$  ( $\text{I}_2$ -free) environment is much faster at  $70^\circ\text{C}$  than at  $25^\circ\text{C}$  (Figure S15b, Supporting Information). The reversal of Rxns. 1 is accelerated significantly as the triple halide ion  $\text{I}_2\text{Br}^-$  is much less stable at  $70^\circ\text{C}$  than at  $25^\circ\text{C}$  (Figure S15c, Supporting Information), which possibly causes the much faster PL recovery at higher temperature (Figure S15b, Supporting Information). Therefore, when the perovskite is under illumination and heating (for example  $70^\circ\text{C}$ ), the photogenerated  $\text{I}_2$  becomes less favorable to react with  $\text{Br}^-$  to form  $\text{I}_2\text{Br}^-$  which possibly contributes to the suppressed photo-induced halide segregation at higher temperature.

It has been shown that the incorporation of  $\text{Cs}^+$  can slow down the photo-induced I-rich phase formation.<sup>[1b]</sup> Here we prepared  $\text{CsPbI}_{1.5}\text{Br}_{1.5}$  perovskite thin film, which shows a more stable PL emission than  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  under the same illumination (Figures 4b and 5a). We further fabricated  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  and  $\text{CsPbI}_{1.5}\text{Br}_{1.5}$  perovskite solar cells in an *n-i-p* device architecture. The photovoltaic parameters recorded with simulated AM1.5G illumination and the external quantum efficiency (EQE) spectra are shown in Figures S8–11 (Supporting Information). The in situ PL measurements were conducted while devices were aged either under open-circuit condition or at a voltage bias of 0.80 times the maximum power point voltage ( $0.80 \times V_{\text{MPP}}$ ) to check for stability under





**Figure 5.** a) PL evolution of the CsPbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite thin film under the illumination of a 405 nm diode with an intensity of 50 mW cm<sup>-2</sup>. b) The feasibility of the reaction in CsBr+I<sub>2</sub> mixture over a duration of 1 week. PL evolution of c) CsPbI<sub>1.5</sub>Br<sub>1.5</sub> and d) CsPbBr<sub>3</sub> perovskite thin films upon I<sub>2</sub> exposure in the dark over 40 min.

representative operating conditions (Shown schematically in Figure S12a, Supporting Information). Under both aging conditions, the CsPbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite thin film shows better stability of the PL (Figures S12b–e, Supporting Information), and in general, of all figures of merit of the solar cell (Figure S13, Supporting Information) than the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> counterpart. I<sub>2</sub> formation in the mixed I-Br perovskite under illumination is the first key step to induce I-rich phase formation. We then checked the I<sub>2</sub> formation in the CsPbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite thin film following the same method used to check that in the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> counterpart. It is found that the I<sub>2</sub> formation rate is identical in CsPbI<sub>1.5</sub>Br<sub>1.5</sub> and Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> thin films under illumination (Figure S14, Supporting Information). Meanwhile, I<sub>2</sub> shows a higher barrier to react with Br<sup>-</sup> in the pure-Cs environment than in the FA-containing environment to form triple halide ion (Figures 2c; Figures S3 and S4, Supporting Information). Therefore, the possible reason that CsPbI<sub>1.5</sub>Br<sub>1.5</sub> has a higher spectral stability than Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> is mainly due to the higher Br<sup>-</sup> binding strength and the suppressed production of I<sup>-</sup> and thus I-rich phase through Rxns. 1 and 2, when the I<sub>2</sub> supply is identical. Please note that the emergence of PL emission at longer wavelengths is still observable in CsPbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite under illumination (Figure 5a), which indicates the I-rich phase formation is not suppressed completely. This is possibly because the reaction between CsBr and I<sub>2</sub> can still happen but in a much slower rate, as after 1 week the CsBr+I<sub>2</sub> mixture shows the formation of dark-red compound (Figure 5b). Furthermore, we also exposed I<sub>2</sub> to CsPbI<sub>1.5</sub>Br<sub>1.5</sub> and CsPbBr<sub>3</sub> thin films, and in both cases the emerging of PL emission at longer

wavelength are visible but are highly suppressed (Figure 5c,d) compared with the Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> and Cs<sub>0.17</sub>FA<sub>0.83</sub>PbBr<sub>3</sub> counterparts (Figures 1d and 3b), respectively. Meanwhile, it is found that mixed I-Br perovskites always show more significant PL redshift than pure-Br counterparts when exposed to I<sub>2</sub>.

To clearly depict the impact of chemical composition on the stability of perovskites phases and the thermodynamics of I<sub>2</sub> incorporation, we carry out density functional theory (DFT) on APbI<sub>3-x</sub>Br<sub>x</sub> compositions (A = FA, MA or Cs; x = 0, 1.5 and 3). We start by calculating the perovskite formation energy ( $\Delta_f H$ , Table 1) from precursors. For a fixed A-site cation, a progressive decrease in stability (more positive  $\Delta_f H$ ) is reported by increasing the iodide content (Table 1), in agreement with reported experimental data.<sup>[36]</sup> For a fixed halide composition, an increase of stability (within the perovskite “black” phase, for tri-iodide samples) is observed moving from FA, MA, and Cs (Table 1), which is consistent with the decrease of the tolerance factor resulting from the smaller cation radius. An additional contribution to the stability of mixed halide (and in general of alloyed) perovskites comes from the entropy of mixing, which at 300 K accounts to a stabilization 0.05 eV per formula unit, see Table 1 and it further increases at higher temperature. Based on these observations and the data shown in Table 1, it is clear that the capability of an electron accepting I<sub>2</sub> molecule to perturb the pristine perovskite structure will be less effective when the iodide content in the perovskite is decreased, as well as when moving to Cs cation. It is significant to notice, looking at the same scenario from an electronic point of view, that the valence band of Cs halide perovskites is typically deeper than that of FA-based counterparts, due to octahedra

**Table 1.** Formation energies of the investigated perovskites starting from precursors ( $\Delta_f H$ ). For mixed halide perovskites the Gibbs formation energies ( $\Delta G = \Delta_f H - T\Delta S$ ) are reported in parenthesis by adding the mixing entropy times 300 K ( $-T\Delta S = -0.05$  eV per f.u.) to  $\Delta_f H$ .  $I_2$  incorporation energy ( $\Delta(E)I_2$ ) calculated as the sum of the defect formation energies of positive  $I_i^+$  and negative  $I_i^-$  iodine interstitials calculated at the VBM of the perovskites in I-rich conditions. Please note that for the lead tri-iodide semiconductors, the formation energy and stability comparisons are done within the perovskite (black) phase.

Phase	$\Delta_f H$ [eV]	$\Delta(E)I_2$ [eV]
FAPbBr <sub>3</sub>	-0.02	0.80
FAPbBr <sub>5/3</sub> I <sub>4/3</sub>	0.08 (0.03)	0.13
FAPbI <sub>3</sub>	0.14	0.30
MAPbBr <sub>3</sub>	-0.13	1.62
MAPbBr <sub>1.5</sub> I <sub>1.5</sub>	0.01 (-0.04)	1.01
MAPbI <sub>3</sub>	0.01	0.86
CsPbBr <sub>3</sub>	-0.31	1.40
CsPbBr <sub>1.5</sub> I <sub>1.5</sub>	-0.16 (-0.21)	0.96
CsPbI <sub>3</sub>	-0.14	0.92

tilting, which can be read as better capability of Cs of keeping halogen electrons more bounded.<sup>[37]</sup>

As previously reported, a  $I_2$  molecular is stable in a combination of a positive and a negative interstitials in the perovskite bulk according to reaction  $I_2 = I_i^+ + I_i^-$ .<sup>[38]</sup> To estimate the incorporation thermodynamics of  $I_2$  in different perovskites, the defect formation energies (DFEs) of the  $I_i^+$  and  $I_i^-$  interstitials was thus calculated and the structures are shown in Figure S16 (Supporting Information). By neglecting defect couple interactions, an estimate of the  $I_2$  incorporation energy is obtained by summing the DFEs of the two interstitials.  $I_2$  incorporation into the perovskite lattice is more favorable in full iodide than full bromide perovskites, by showing a monotonic trend moving between the two extrema, except for the mixed-halide FA perovskite. By comparing the different cations,  $\Delta(E)I_2$  increases following the sequence of FA, MA, and Cs. Overall, the observed trend indicates that  $I_2$  incorporation is more favorable in FA-based perovskites, which are the least stable composition examined here. Using cations with smaller radius ( $Cs^+$ ) increases the lattice stability and reduces the tendency to incorporate the electron accepting  $I_2$  molecule.

### 3. Conclusions

In summary, we demonstrated how  $I_2$  formed through photo-carrier trappings at interstitial iodide defects can cause bandgap photo-instability in the mixed I-Br perovskite. Specifically,  $I_2$  undergoes a redox process to react with  $Br^-$  to form  $I_2Br^-$  ( $I^{\delta-}-I^{\delta+}-Br^{\delta-}$ ), whose negatively charge iodide ( $I^{\delta-}$ ) can further exchange with another lattice  $Br^-$  and leads to the formation of I-rich phase. Such a process is regulated by the binding strength of  $Br^-$  in the perovskite. These findings allow to describe the process behind the photo-instability of mixed I-Br perovskites and rationalize a variety of experimental observation. For example, it has been re-

ported that monovalent cations of rubidium ( $Rb^+$ )<sup>[39]</sup> and potassium ( $K^+$ )<sup>[40]</sup> also help to suppress halide segregation. This observation also agrees with our model as  $Rb^+$  and  $K^+$  have smaller sizes and thus higher charge density than  $FA^{+26}$  and should have identical role as  $Cs^+$  to increase the binding strength of  $Br^-$  in the perovskite. We provide a new insight to rationalize the role of the chemical composition of the perovskite unit cell, which not only aims at the reduction of native defects causing  $I_2$  formation, but also looks at the improvement of the binding strength of  $Br^-$  by introducing cations with higher charge density in the perovskite.

### 4. Experimental Section

**Substrate Cleaning:** Fluorine-doped tin oxide (FTO)-coated glass was etched with zinc powder and 2 M aqueous HCl solution for electrode pattern. The FTO and glass substrates were washed with 2% Hellmanex in water, deionized water, iso-propanol, acetone, and iso-propanol subsequently in a sonication bath for 15 min.

For the solar cells used for the in situ PL and  $J$ - $V$  measurement at a voltage bias of  $0.8 \times V_{MPP}$ , patterned indium tin oxide (ITO) covered glass substrates were used. The substrates were cleaned by sonicating in an acetone bath, scrubbing and sonicating in an aqueous solution of dodecyl sodium sulphate (Acros, 99%). After rinsing in deionized water, substrates were sonicated in 2-propanol. The substrates were dried and treated with UV-ozone for 30 min.

**Preparation of Electron Transporting Layer:** The  $SnO_2$  colloid precursor was obtained from Alfa Aesar (tin(IV) oxide, 15% in  $H_2O$  colloidal dispersion). Before use, the  $SnO_2$  colloid precursor was mixed with water in a volume ration of 1:5.67. The FTO substrates were treated by  $O_2$  plasma cleaning for 10 min before depositing of  $SnO_2$ . The diluted  $SnO_2$  colloid solution was spin coated onto FTO substrates at 3000 rpm for 30 s, and then baked on a hotplate in ambient air (humidity  $\approx 70\%$  RH, temperature  $\approx 22^\circ C$ ) at  $120^\circ C$  for 10 min, followed by 30 min at  $180^\circ C$ . After annealing, the hotplate was switched off, and the FTO substrates were allowed to cool down to room temperature naturally. Subsequently, the substrates were treated by UV-ozone for 15 min and then transferred to a  $N_2$  filled glovebox.

For the solar cells used for the in situ PL and  $J$ - $V$  measurement at a voltage bias of  $0.8 \times V_{MPP}$ , the electron transporting layer is prepared as follows. The  $SnO_2$  colloid precursor was obtained from Alfa Aesar (tin(IV) oxide, 15wt.% in  $H_2O$  colloidal dispersion). Before use, the  $SnO_2$  colloid precursor was mixed with water in a volume ratio of 1:5. The  $SnO_2$  dispersion was spin-coated onto the ITO/glass substrates at 2800 rpm (with a  $2000\text{ rpm}^{-1}$  s acceleration) for 60 s and dried at  $150^\circ C$  for 30 min in an ambient atmosphere. The  $SnO_2$  film was treated with UV-ozone for 10 min and then quickly transferred into a nitrogen-filled glovebox. A layer of PCBA was deposited before depositing perovskite. The [6,6]-phenyl- $C_{61}$ -butyric acid (PCBA), dissolved in 1,2-dichlorobenzene (DCB, Sigma-Aldrich, anhydrous 99%) at  $0.1\text{--}0.2\text{ mg mL}^{-1}$  and stirred at  $60^\circ C$ , was spin-coated onto the  $SnO_2$  substrate at 2000 rpm (with a  $3000\text{ rpm}^{-1}$  s acceleration) for 30 s.

**Material Fabrication:** The precursor of  $Cs_{0.17}FA_{0.83}Pb_{1.5}Br_{1.5}$  perovskite was prepared by mixing 0.17 M CsI (Alfa-Aesar 99.999%), 0.83 M FAI (Great Solar), 0.25 M  $PbI_2$  (TCI, 99.99%) and 0.75 M  $PbBr_2$  (TCI, >98%) in anhydrous DMF: DMSO 4:1 (v:v) and stirred overnight. The precursor of  $Cs_{0.17}FA_{0.83}PbBr_3$  was prepared by mixing 0.085 M CsBr (Alfa-Aesar, 99.999%), 0.415 M FABr (Great Solar) and 0.5 M  $PbBr_2$  (TCI, >98%) in anhydrous DMF: DMSO 4:1 (v:v) and stirred overnight. The precursor of FAPbBr<sub>3</sub> was prepared by mixing 0.5 M FABr (Great Solar) and 0.5 M  $PbBr_2$  (TCI, >98%) in anhydrous DMF: DMSO 4:1 (v:v) and stirred overnight. The precursor of  $CsPbI_{1.5}Br_{1.5}$  was prepared by mixing 1 M CsI (Alfa-Aesar, 99.999%), 0.25 M  $PbI_2$  (TCI, 99.99%) and 0.75 M  $PbBr_2$  (TCI, >98%) in anhydrous DMSO. The precursor of CsPbBr<sub>3</sub> was prepared by mixing 0.5 M CsBr (Alfa-Aesar, 99.999%) and 0.5 M  $PbBr_2$  (TCI, >98%) in anhydrous DMSO. The thin films were deposited by spin-coating on the glass

substrates in a two-step procedure at 1000 rpm and 5000 rpm for 10 s and 40 s respectively. During the second step, 120  $\mu\text{L}$  of chlorobenzene was casted onto the substrates 10 s before the ending of the second spinning step. The films were placed on a hotplate at 100  $^{\circ}\text{C}$  for 30 min. The perovskite powders were obtained by scratching off the thin films from the glass.

For the  $\text{CsPbI}_{1.5}\text{Br}_{1.5}$  solar cells used for the in situ PL and J-V measurement at a voltage bias of  $0.8 \times V_{\text{MPP}}$ , the precursor was prepared by mixing 0.87 M CsI (Sigma-Aldrich, 99.999%), 0.22 M  $\text{PbI}_2$  (TCI, 99.99%) and 0.65 M  $\text{PbBr}_2$  (TCI, >98.0%) in anhydrous DMF:DMSO 1:1.89 (v:v). The precursor was spin-coated onto the glass substrates in a two-step procedure at 600 rpm and 4000 rpm for 5 s and 30 s, respectively. During the second step, 200  $\mu\text{L}$  of methyl acetate was cast onto the substrates 10 s before the ending of the second spinning step. The films were subsequently placed on a hotplate at 35  $^{\circ}\text{C}$  for 5 min, at 120  $^{\circ}\text{C}$  for 10 min, and at 160  $^{\circ}\text{C}$  for 5 min. For the  $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.5}\text{Br}_{1.5}$  solar cells used for the in situ PL and J-V measurement at a voltage bias of  $0.8 \times V_{\text{MPP}}$ , the precursor and the spin-coating procedure was the same as described above, except for the use of ethyl acetate instead of chlorobenzene as antisolvent. The preparation of perovskite thin films for solar cells was performed in a  $\text{N}_2$ -purged glovebox ( $\text{H}_2\text{O} < 10$  ppm and  $\text{O}_2 < 5$  ppm).

**Preparation of Hole Transport Layer and Au Electrode:** The hole-transport layer precursor was prepared by dissolving 72.3 mg spiro-MeOTAD (Luminescence Technology, 99.9%), 28  $\mu\text{L}$  4-tert-butylpyridine (Sigma-Aldrich, 96%) and 17.5  $\mu\text{L}$  bis(trifluoromethane)sulfonimide lithium salt (Sigma-Aldrich) solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1 mL chlorobenzene. The precursor was then spin-coated on the perovskite layer at 4000 rpm for 30 s. The deposition of the hole transport layer was in a glovebox. The solar cells were then transferred to a box with dry air (humidity lower than 20% RH) for oxidation for 16 h. Finally, a 100 nm Au electrode layer was deposited under a vacuum of  $< 1 \times 10^{-4}$  Pa with a rate of 0.1  $\text{nm}^{-1}$  s. The preparation of the Au electrode was performed in a  $\text{N}_2$ -purged glovebox.

For the solar cells used for the in situ PL and J-V measurement at a voltage bias of  $0.8 \times V_{\text{MPP}}$ , the spiro-OMeTAD (80 mg) (Lumtec, 99.5%) was dissolved in chlorobenzene (1 mL) with 4-tert-butylpyridine (28.5  $\mu\text{L}$ ) (Sigma-Aldrich, 99.5%) and bis(trifluoromethylsulfonyl)amine lithium salt (16.6  $\mu\text{L}$ ) (Sigma-Aldrich, 99.95% trace metal basis) of a solution (500 mg  $\text{mL}^{-1}$ ) in acetonitrile (Sigma-Aldrich, anhydrous 99.8%) at 60  $^{\circ}\text{C}$ . Before the deposition, tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (20  $\mu\text{L}$ ) (Greatcell Solar) of a solution (500 mg  $\text{mL}^{-1}$ ) in acetonitrile was added to the Spiro-OMeTAD solution. The chemically doped Spiro-OMeTAD solution was dynamically spin-coated onto the perovskite layer at 2000 rpm (with a 20 000  $\text{rpm}^{-1}$  s acceleration) for 50 s. The sample was then exposed to dry air for 20 min, before being transferred back into the glovebox. Finally,  $\text{MoO}_3$  (10 nm) and Au (100 nm) were sequentially evaporated under high vacuum ( $\approx 3 \times 10^{-7}$  mbar).

**$\text{I}_2$  Vapor Exposure to Perovskite Films:** The  $\text{I}_2$ -vapor exposure experiments were done in a  $\text{N}_2$ -filled glove box ( $\text{H}_2\text{O} < 10$  ppm and  $\text{O}_2 < 5$  ppm) under dark or illumination. The dark is realized by covering the vial loaded with perovskite samples with Al foils. The illumination is provided by a 405 nm diode laser with an intensity of 50  $\text{mW m}^{-2}$ . 20 mg of  $\text{I}_2$  beads (Sigma-Aldrich, 99.99%) was placed in a vial with a height of 10 cm and a diameter 1.5 cm, which was placed on a hot plate. To expose the sample to  $\text{I}_2$  vapor, we heated the vial loaded with  $\text{I}_2$  pellet at 50  $^{\circ}\text{C}$ , while covering the vial with perovskite sample. Since the vial is 10 cm long, we can realize heating only the  $\text{I}_2$  pellet to produce  $\text{I}_2$  vapor while keeping the perovskite sample at an ambient temperature of 22  $^{\circ}\text{C}$ . This means the sample suffered only from  $\text{I}_2$ -vapor exposure, and the possible effect due to sample heating (for example, decomposition) was minimized.

**Triple Halide Ion Formation:** The mixture of CsBr (Alfa-Aesar, 99.999%), FABr (Great Solar) and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) was prepared by mixing them in a mole ratio of 0.17: 0.83: 1. The mixture of CsBr (Alfa-Aesar, 99.999%) and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) is prepared by mixing them in a mole ratio of 1: 1. The mixture of FABr (Great Solar) and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) was prepared by mixing them in a mole ratio of

1: 1. The mixture of FAI (Great Solar) and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) was prepared by mixing them in a mole ratio of 1: 1. The mixture of FABr (Great Solar) and IBr (Sigma-Aldrich, >98%) was prepared by mixing them in a mole ratio of 1: 1. The mixture of  $\text{FAPbBr}_3$  powder and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) were prepared by mixing them in a mole ratio of 1: 1. The preparation of the mixture was conducted in a glovebox filled with  $\text{N}_2$ . The mixture of  $\text{CsPbBr}_3$  powder and  $\text{I}_2$  (Sigma-Aldrich, 99.99%) were prepared by mixing them in a mole ratio of 1: 1. The preparation of the mixture was conducted in a glovebox filled with  $\text{N}_2$ .

**$\text{I}_2$  Formation Test:** Each of the perovskite thin film on glass substrate was sealed in an 8 mL vial filled with 6 mL anhydrous toluene. The vial was further sealed with a plastic bag in  $\text{N}_2$ -filled glovebox. The vial was put under simulated 1 sun illumination provided by a white LED array over 1 to 3 h at 30  $^{\circ}\text{C}$ .

**Measurement and Characterizations:** The X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance equipped with a  $\text{Cu K}\alpha 1$  ( $\lambda = 1.544060 \text{ \AA}$ ) anode, operating at 40 kV and 40 mA. UV-Vis absorption spectra were recorded with a UV-Vis Varian Cary 5000. PL measurements were conducted by using a 405 nm laser with an intensity of 50  $\text{mW cm}^{-2}$ . The PL was acquired with a Maya 2000 pro spectrometer from Ocean Optics. Raman spectra (Renishaw) were measured by using a 785 nm laser. The light source was particularly selected to avoid the PL signal and photochemical degradation that were known to be an issue when performing Raman spectroscopy on halide perovskites. X-ray Photoelectron Spectroscopy (XPS) analyses were performed to evaluate the chemical composition of the materials under investigation. The measurements were carried out with a Kratos Axis Ultra<sup>DLD</sup> spectrometer. High-resolution spectra were acquired at a pass energy of 10 eV using a monochromatic Al  $\text{K}\alpha$  source (15 kV, 20 mA), over the binding energy regions typical for Cs 3d, I 3d, N 1s, C 1s, Pb 4f, and Br 3d peaks.

The current density – voltage (J-V) characteristics of the solar cells were measured with a computer-controlled Keithley 2420 source meter in the air with device encapsulation. The simulated Air Mass 1.5 Global (AM 1.5G) irradiance was provided with a class AAA Newport solar simulator. The light intensity was calibrated with a silicon reference cell with a spectral mismatch factor of 0.99. The active area of the complete device was determined by an illumination-shadowing mask which is 0.0935  $\text{cm}^2$ . For the J-V measurement, the scan rate was 0.05  $\text{V s}^{-1}$  for the slow scan. The forward scan started from 0 V (the short circuit condition) to 1.4 V, while the reverse scan was from 1.4 to 0 V. Preconditioning stress was not done for PV measurements.

For the solar cells used for the in situ PL and J-V measurement at a voltage bias of  $0.8 \times V_{\text{MPP}}$ , J-V characteristics were measured in the glovebox by a Keithley 2400 source measure unit (SMU). A tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter was used to simulate AM1.5G 100  $\text{mW cm}^{-2}$  solar light. A black shadow mask with an aperture area of 0.0676 or 0.1296  $\text{cm}^2$  was used to define the illuminated cell area. EQE spectra were recorded with a home-built set up using light of a tungsten-halogen lamp (Philips focusline, 50 W) that was modulated by a mechanical chopper (Stanford Research, SR 540) before passing into a monochromator (Oriel, Cornerstone 130). The spectral response of the device was recorded as a voltage from a pre-amplifier (Stanford Research, SR 570) using a lock-in amplifier (Stanford Research, SR 830), and was calibrated by a reference silicon cell. A green diode laser (530 nm, Thorlabs M530L3, driven by a DC4104 driver) was used as a light bias to provide the solar cell with approximately one sun illumination intensity during the measurement.

To record PL and  $V_{\text{OC}}$  data simultaneously during continuous illumination (405 nm, 50  $\text{mW cm}^{-2}$ ) in open circuit condition, the solar cells are mounted in a Arkeo stability platform (Cicci Research, Italy) with  $\text{N}_2$  flow (temperature  $\approx 27^{\circ}\text{C}$ ). All the cells were encapsulated before stability test.

To record PL and J-V data simultaneously during continuous illumination, the solar cells were mounted in a custom-built holder to maintain an inert environment. The device area was defined by a shadow mask (0.16  $\text{cm}^2$  aperture) and the cell was connected to a Keithley 2400 source measure unit (SMU). A 405 nm diode laser (Thorlabs M405L4 diode laser driven by Thorlabs DC4104 driver) was used to illuminate the sample at an intensity determined by comparing the current output to the short-



circuit current density measured under AM1.5G 1-Sun illumination (circa  $50 \text{ mW m}^{-2}$ ). The photoluminescence light (filtered by a 455 nm long pass filter) was focused on an optical fiber and recorded using a spectrometer (Avantes Avaspec – 2048x14). The SMU and spectrometer were operated on a custom-built LabVIEW code. Reverse and forward voltage scans were sequentially conducted between +1.25 and –0.2 V at a rate of  $0.12 \text{ V s}^{-1}$ , followed by acquisition of a photoluminescence spectrum from the active area of the solar cell while the cell was held in open-circuit. In between measurements, the cells were continuously illuminated and held below the maximum power point voltage ( $V_{\text{MPP}}$ ) at  $0.8 \times V_{\text{MPP}}$ , where  $V_{\text{MPP}}$  was determined from the reverse current density – voltage scan under AM1.5G illumination. The cycle ( $J$ - $V$  scan, PL measurement, delay) was repeated for a pre-set duration. The measurements were conducted at room temperature without active temperature control. The  $V_{\text{MPP}}$  was  $\approx 0.8 \text{ V}$  for CsFA-perovskite and  $\approx 0.9 \text{ V}$  for Cs-perovskite. By going to  $0.8 \times V_{\text{MPP}}$ , it was ensured that charges will be extracted also when the  $V_{\text{MPP}}$  would be slightly reduced during the illumination. Figure S14 (Supporting Information) shows that at  $0.8 \times 0.8 \text{ V} = 0.64 \text{ V}$  (for CsFA) and  $0.8 \times 0.9 \text{ V} = 0.72 \text{ V}$  (for Cs) we remain in the part of the  $J$ - $V$  curve where photocurrent changes slightly with a small offset from  $V_{\text{MPP}}$ . Hence we could be sure that we extracted the carriers.

**Computational Detail:** DFT calculations were carried out in periodic boundary conditions by using the Quantum Espresso simulation package.<sup>[41]</sup> The equilibrium structures of the different phases were found by relaxing both ion positions and cell parameters. Specifically, starting from the experimental structures of the full bromide perovskites (FAPbBr<sub>3</sub> trigonal,<sup>[42]</sup> MAPbBr<sub>3</sub> tetragonal,<sup>[43]</sup> CsPbBr<sub>3</sub> orthorhombic<sup>[44]</sup>), bromide ions were progressively substituted by iodides in order to form the mixed and full iodide perovskites. In all cases full relaxations of ion positions and cell parameters were performed. DFT calculations were conducted by using the Perdew-Burke-Ernzerhof (PBE) functional<sup>[45]</sup> and by including DFTD3 dispersion corrections.<sup>[46]</sup> Norm-conserving pseudopotentials<sup>[47]</sup> (I 5s, 5p; Br 4s, 4p; N and C 2s, 2p; H 1s; Pb 5d, 6s, 6p shells explicitly included) with a cutoff of 60 Ry on the wavefunctions and converged k-point grids were used.

Interstitial iodines have been simulated in the  $2 \times 2 \times 2$  supercells of the optimized phases with the same computational setup described above and by sampling the Brillouin zone (BZ) at the  $\Gamma$  point. Relaxation of defect structures was performed by fixing cell parameters to the optimized values. DFEs and TILs were calculated according to the expressions<sup>[48]</sup>:

$$DFE [I_i^q] = E [I_i^q] - E [perf] - \mu_I + q (\epsilon_{\text{VB}} + \epsilon_F) + E_{\text{corr}}^q \quad (5)$$

$$\epsilon (q/q') = \frac{E [I_i^q] - E [I_i^{q'}]}{q' - q} + \frac{E_{\text{corr}}^q - E_{\text{corr}}^{q'}}{q' - q} - \epsilon_{\text{VB}} \quad (6)$$

where the term  $E [I_i^q]$  is the energy of the supercell with interstitial in charge state  $q$ ,  $E [perf]$  is the energy of the perfect supercell,  $\mu_I$  is the chemical potentials of iodine  $\mu(\text{I}) = \frac{1}{2} \mu(\text{I}_2\text{-solid})$ ,  $\epsilon_{\text{VB}}$  is the valence band energy,  $\epsilon_F$  and  $E_{\text{corr}}^q$  the Fermi level of the system and corrections due to periodic charges. Makov-Payne correction terms were applied considering a mean static dielectric constants  $\epsilon_0 = 22$ , estimated by averaging the values for the pure bromide and iodide phases.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

defects, metal halide semiconductors, optoelectronics, solar cells, wide bandgap metal halide perovskites

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