Supporting Information

For

Effect of Formamidinium (FA) ions on the Mixed ‘A’-site Based Bromide Perovskite (APbBr₃) Thin Films

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S1 Goldsmith’s Tolerance factor (t) and Octahedral Factor (μ)

\[ t = \frac{r_{A_{\text{effective}}} + r_{Br^{-}}}{\sqrt{2} (r_{Pb^{2+}} + r_{Br^{-}})} \]

\[ \mu = \frac{r_{Pb^{2+}}}{r_{Br^{-}}} \]

For PbBr₆⁴⁻ octahedra, the ‘μ’ value is 0.607. To form stable BX₆ octahedra, ‘μ’ should be between 0.442 to 0.895. Also, the ‘t’ value for FA₀.₅MA₀.₄Cs₀.₁PbBr₃ is 0.961 and that for MA₀.₉Cs₀.₁PbBr₃ is 0.92. For perovskites to follow a cubical structure, ‘t’ should be between 0.813 to 1.107.
XRD after CV analysis

Fig. S1 XRD after CV within electrochemical stability window (1.5 V to -0.8 V) and beyond stability window (2.5 V to -2.5 V) of a) MA$_{0.9}$Cs$_{0.1}$PbBr$_3$ and b) FA$_{0.5}$MA$_{0.4}$Cs$_{0.1}$PbBr$_3$ perovskites.

S2 Formal Potential and HOMO level determination from CV

To calibrate the electrochemical system and determine the formal potential, 1.9 mM ferrocene was dissolved in the solvent-electrolyte mixture. The corresponding CV was measured with blank FTO using Ag/AgCl reference electrode and Pt counter electrode. We determined The formal potential by taking the average of both oxidation (1.07 V) and reduction peak potentials (-0.24 V), as shown in Fig. S2a. The HOMO energy level of both HOIPs was determined by the oxidation potential generated from the CV peak.
The equation is $E_{\text{HOMO}} = -[(E_{\text{ox}} - E_{1/2\text{ferrocene}}) + 4.8] \text{ eV}$, where $E_{\text{ox}}$ is the oxidation peak potential and $E_{1/2\text{ferrocene}}$ is the formal potential obtained$^2$. In comparison, Fc/Fe$^+$ redox reference and 4.8 eV is the HOMO energy level of ferrocene, which is already known.

Formal potential,

$$E_{(1/2)} = \frac{1}{2} [E_{p(o)} + E_{p(r)}]$$

$$E(1/2) = \frac{1}{2} [1.07 + (-0.24)]$$

$$= -0.41 \text{ V}$$

HOMO energy level of FA$_{0.3}$MA$_{0.4}$Cs$_{0.1}$PbBr$_3$,

$$\text{FA}_{0.3}\text{MA}_{0.4}\text{Cs}_{0.1}\text{PbBr}_3$$

$$E_{(\text{HOMO})} = -[(E_{\text{ox}} - E_{1/2\text{ferrocene}}) + 4.8]$$

$$= -[1.29 - 0.41] + 4.8$$

$$= -5.68 \text{ eV}$$

HOMO energy level of MA$_{0.9}$Cs$_{0.1}$PbBr$_3$,

$$\text{MA}_{0.9}\text{Cs}_{0.1}\text{PbBr}_3$$

$$E_{(\text{HOMO})} = -[(E_{\text{ox}} - E_{1/2\text{ferrocene}}) + 4.8] \text{ eV}$$

$$= -[1.21 - 0.41] + 4.8$$

$$= -5.60 \text{ eV}$$
Fig. S3: a) I-V curve b) EQE of Perovskite solar cell devices made of both FA$_{0.5}$MA$_{0.4}$Cs$_{0.1}$PbBr$_3$ and MA$_{0.9}$Cs$_{0.1}$PbBr$_3$ perovskites. c) SEM image showing perovskite solar cell cross-section.

Fig. S4: Time-resolved PL data of both FA$_{0.5}$MA$_{0.4}$Cs$_{0.1}$PbBr$_3$ and MA$_{0.9}$Cs$_{0.1}$PbBr$_3$ perovskites. The average lifetime ($\tau$) of FA$_{0.5}$MA$_{0.4}$Cs$_{0.1}$PbBr$_3$ perovskite is 124 ps and that of MA$_{0.9}$Cs$_{0.1}$PbBr$_3$ perovskites is 85 ps.
**Table S1** Atomic % ratio of Cs, Pb and Br elements in perovskite thin films

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<th>Perovskite Composition</th>
<th>Atomic % (±4%) Cs: Pb: Br</th>
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<tr>
<td>FA&lt;sub&gt;0.5&lt;/sub&gt;MA&lt;sub&gt;0.4&lt;/sub&gt;Cs&lt;sub&gt;0.1&lt;/sub&gt;PbBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.4: 28.2: 68.1</td>
</tr>
<tr>
<td>MA&lt;sub&gt;0.9&lt;/sub&gt;Cs&lt;sub&gt;0.1&lt;/sub&gt;PbBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.7: 28.1: 68.5</td>
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**Table S2** Perovskite solar cell device parameters.

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<tr>
<th>HTM</th>
<th>Perovskite Composition</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (η)</th>
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<tr>
<td>PTAA</td>
<td>FA&lt;sub&gt;0.5&lt;/sub&gt;MA&lt;sub&gt;0.4&lt;/sub&gt;Cs&lt;sub&gt;0.1&lt;/sub&gt;PbBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.67</td>
<td>-3.22</td>
<td>51.1</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>MA&lt;sub&gt;0.9&lt;/sub&gt;Cs&lt;sub&gt;0.1&lt;/sub&gt;PbBr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.62</td>
<td>-2.71</td>
<td>53.59</td>
<td>0.9</td>
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**Notes and references:**
