Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

For

Effect of Formamidinium (FA) ions on the Mixed 'A'-site Based Bromide Perovskite ($APbBr_3$) Thin Films

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

$$t = \frac{rA_{effective} + rBr^-}{\sqrt{2}\,(rPb^{2+} + rBr)}$$

$$\mu = \frac{rPb^{2+}}{rBr^-}$$

For $PbBr_6^{4-}$ octahedra, the 'μ' value is 0.607. To form stable BX_6 octahedra, 'μ' should be between 0.442 to 0.895. Also, the 't' value for $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ is 0.961 and that for $MA_{0.9}Cs_{0.1}PbBr_3$ is 0.92. For perovskites to follow a cubical structure, 't' should be between 0.813 to 1.107.

XRD after CV analysis

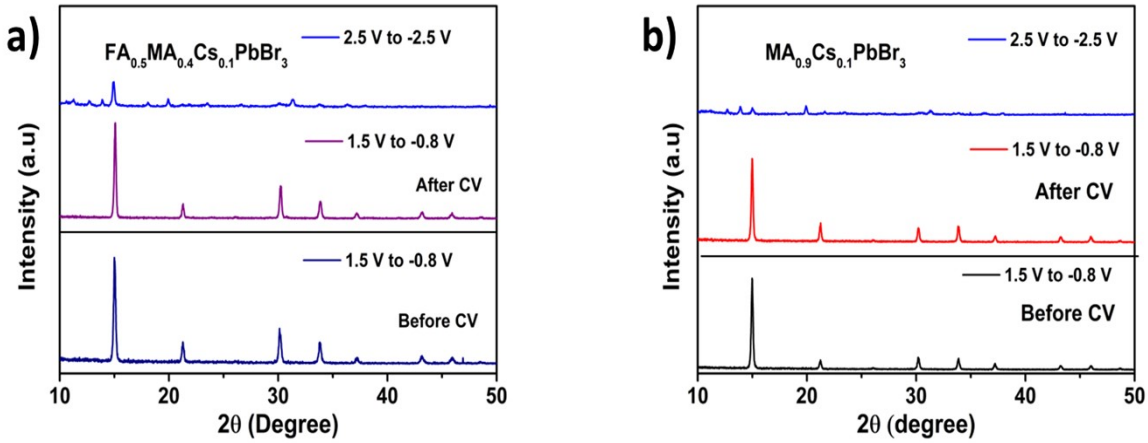

Fig. S1 XRD after CV within electrochemical stability window (1.5 V to -0.8 V) and beyond stability window (2.5 V to -2.5 V) of **a)** $MA_{0.9}Cs_{0.1}PbBr_3$ and **b)** $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ perovskites.

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.[1] 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.

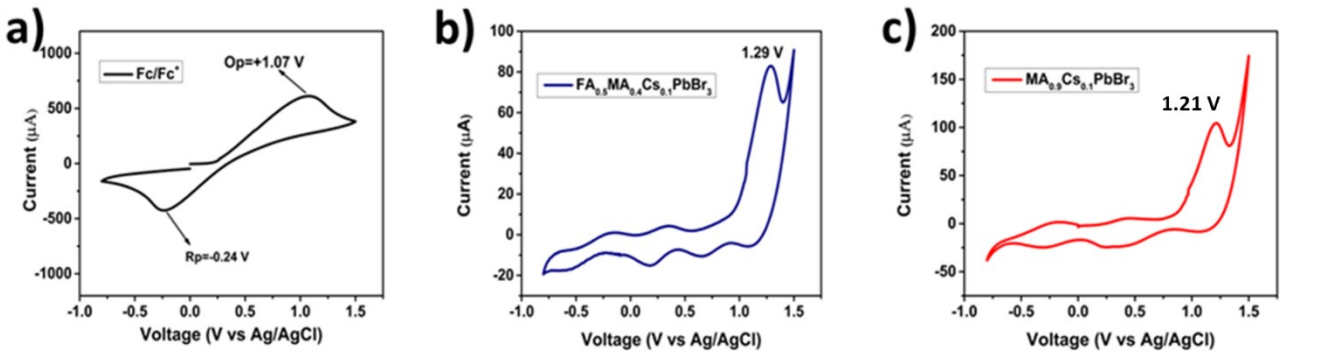

Fig. S2 CV plots of **a)** Fc/Fc^+ redox couple **b)** $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ **c)** $MA_{0.9}Cs_{0.1}PbBr_3$ perovskites

The equation is E_{HOMO}=-e[($E_{(ox)}$-E1/2$_{ferrocene}$) +4.8] eV, where 'e' is the electronic charge, $E_{(ox)}$ is the oxidation peak potential and E1/2$_{ferrocene}$ is the formal potential obtained[2]. In comparison, Fc/Fc^+ redox reference and 4.8 eV is the HOMO energy level of ferrocene, which is already known.

Formal potential,

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

$$E(1/2)=1/2[1.07+(-0.24)]$$

$$=0.41\ V$$

HOMO energy level of $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$,

$$E_{(HOMO)} = -e[(E_{(ox)}-E1/2_{(ferrocene))} +4.8]$$

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

$$= -5.68\ eV$$

HOMO energy level of $MA_{0.9}Cs_{0.1}PbBr_3$,

$$E_{(HOMO)} = -e[(E_{(ox)}-E1/2_{(ferrocene))} +4.8]$$

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

$$= -5.60\ eV$$

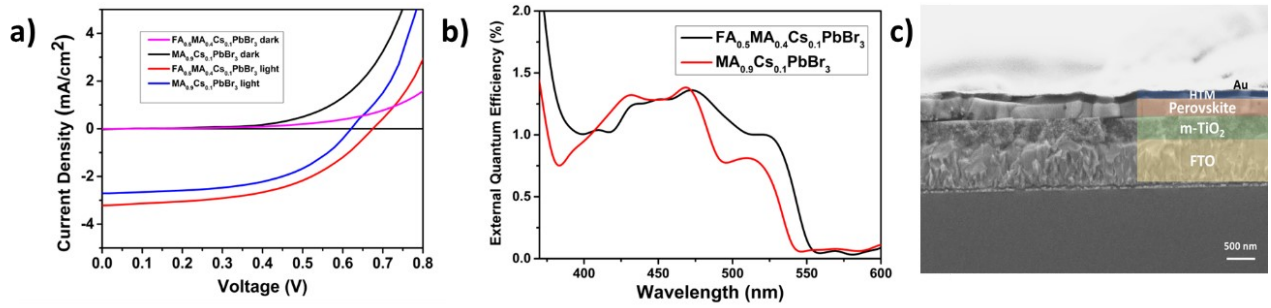

Fig. S3 a) I-V curve **b)** EQE of Perovskite solar cell devices made of both $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ and $MA_{0.9}Cs_{0.1}PbBr_3$ perovskites. **c)** SEM image showing perovskite solar cell cross-section.

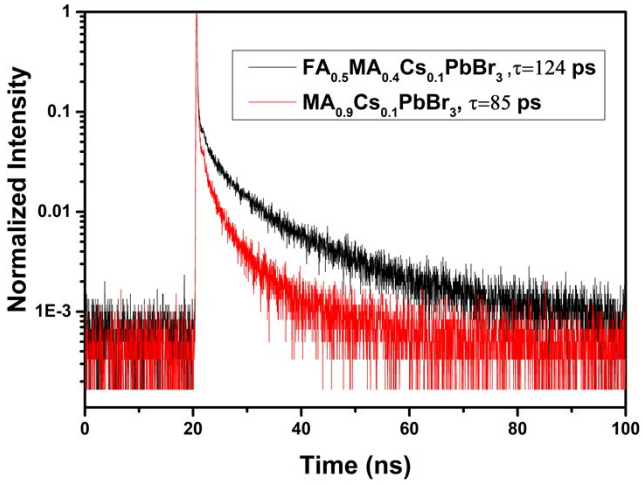

Fig. S4: Time-resolved PL data of both $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ and $MA_{0.9}Cs_{0.1}PbBr_3$ perovskites.The average lifetime (τ) of $FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$ perovskite is 124 ps and that of $MA_{0.9}Cs_{0.1}PbBr_3$ perovskites is 85 ps.

Table S1 Atomic % ratio of Cs, Pb and Br elements in perovskite thin films

Perovskite Composition	Atomic % (±4%) Cs: Pb: Br
$FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$	3.4: 28.2: 68.1
$MA_{0.9}Cs_{0.1}PbBr_3$	3.7: 28.1: 68.5

Table S2 Perovskite solar cell device parameters.

HTM	Perovskite Composition	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill Factor (%)	Efficiency (η)
PTAA	$FA_{0.5}MA_{0.4}Cs_{0.1}PbBr_3$	0.67	-3.22	51.1	1.11
	$MA_{0.9}Cs_{0.1}PbBr_3$	0.62	-2.71	53.59	0.9

Notes and references:

1 D. Cardenas-Morcoso, A. F. Gualdrón-Reyes, A. B. Ferreira Vitoreti, M. García-Tecedor, S. J. Yoon, M. Solis de la Fuente, I. Mora-Seró and S. Gimenez, *J Phys Chem Lett*, 2019, **10**, 630–636.

2 A. Shafiee, M. Mat Salleh and M. Yahaya, *Sains Malays*, 2011, **40**, 173–176.