Electronic supplementary information

Europium shuttle for launching perovskites to space: using Eu^{2+}/Eu^{3+} redox chemistry to boost photostability and radiation hardness of complex lead halides

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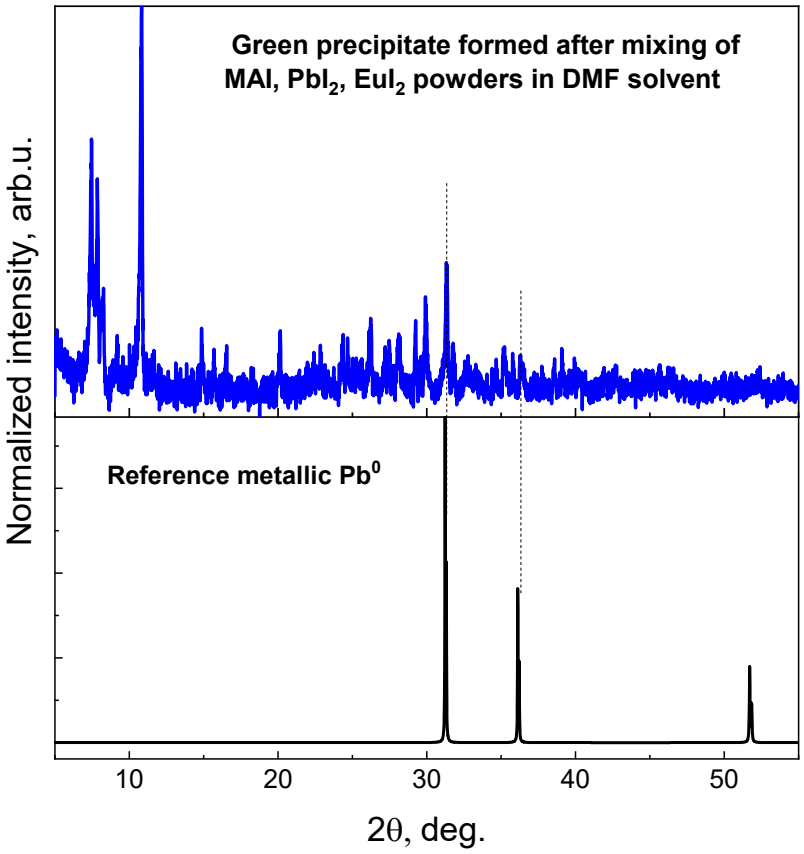

Figure S1. The XRD pattern of the precipitate formed upon interaction of Eu^{2+} with Pb^{2+} in the presence of MAI and DMF solvent.

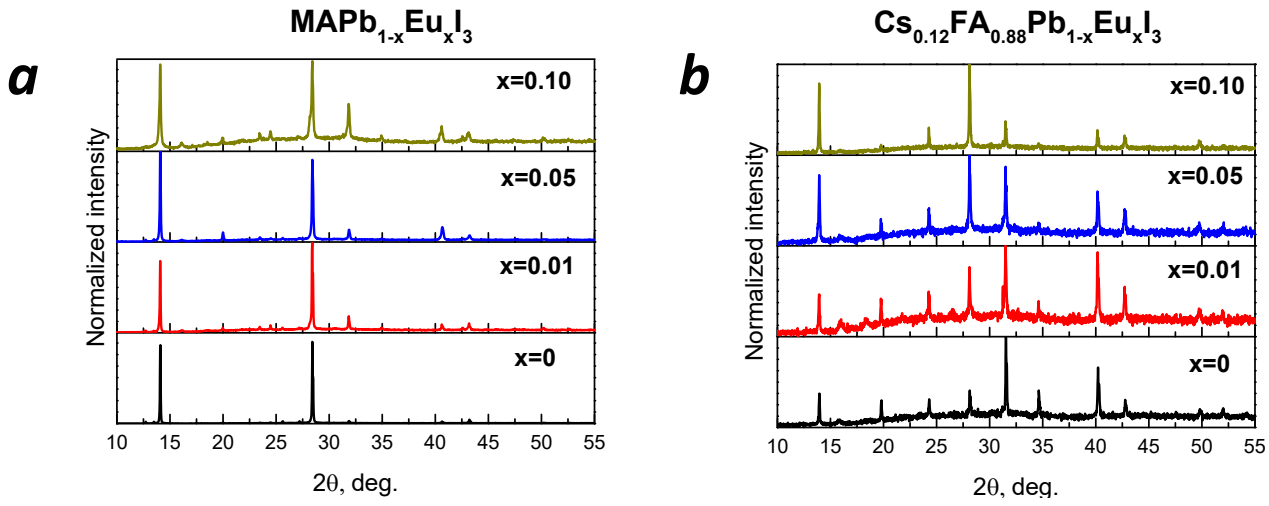

Figure S2. XRD patterns of $MAPb_{1-x}Eu_xI_3$ and $Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ films with different Eu loadings.

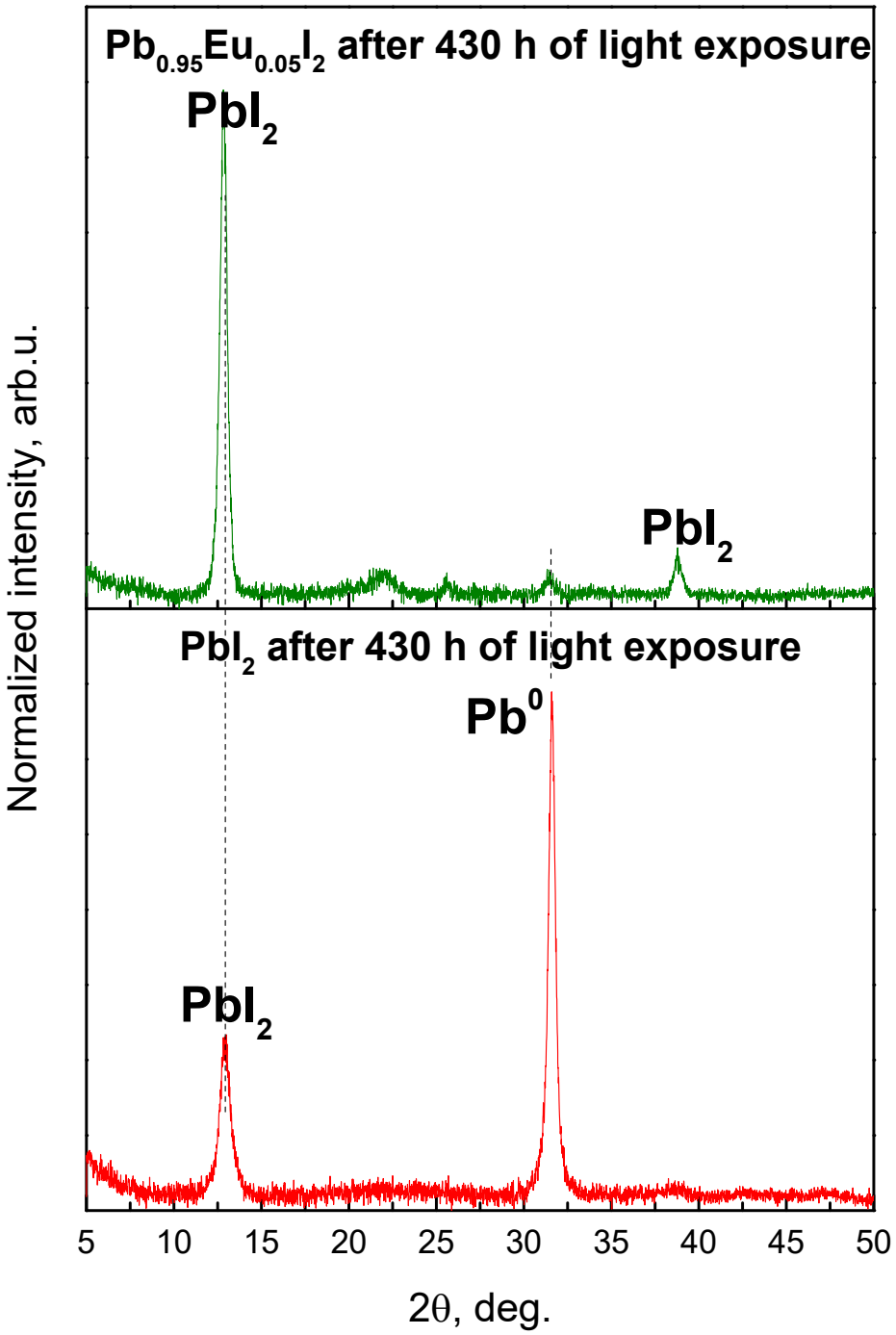

Figure S3. The XRD patterns of the PbI_2 films with (top) and without (bottom) Eu modification after 430 hours of exposure to light (85 mW/cm^2, 32 ^{o}C).

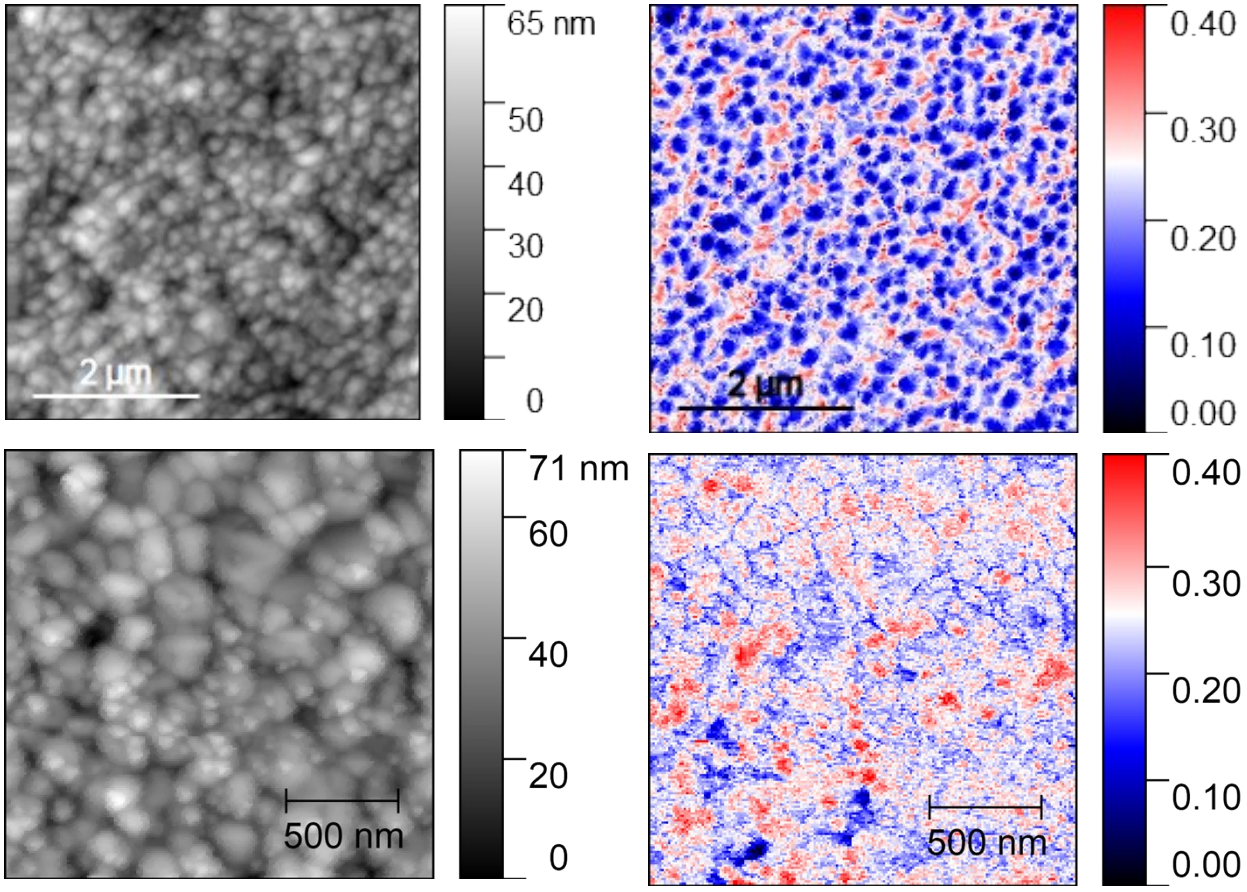

Figure S4. AFM topography (left column) and IR s-SNOM images taken at the FA characteristic vibration frequency for $Cs_{0.12}FA_{0.88}PbI_3$ films after exposure to 1×10^{16} e/cm^2 fluence of 8.5 MeV electrons. The images are presented with 5×5 µm (top) and 2×2 µm (bottom) scalebars to show that the newly formed grains on the surface are enriched with FA cations.

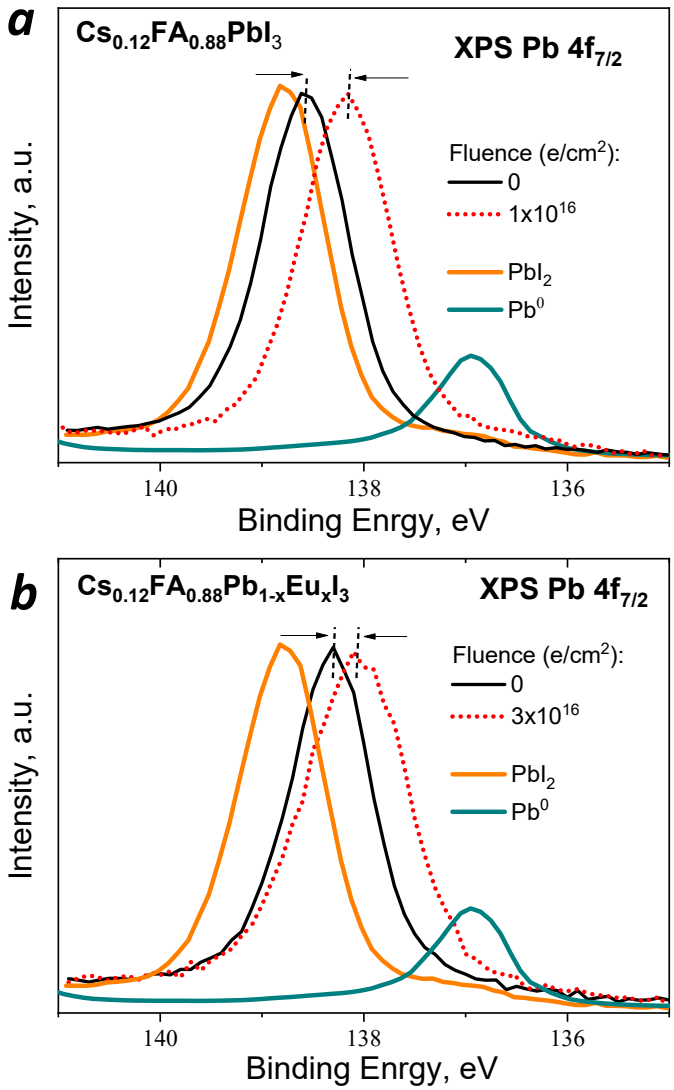

Figure S5. The XPS analysis of the $Cs_{0.12}FA_{0.88}PbI_3$ and $Cs_{0.12}FA_{0.88}Pb_{0.999}Eu_{0.001}I_3$ films before and after the exposure of high-energy electrons ($1 \cdot 10^{16}$ and $3 \cdot 10^{16}$ $e \cdot cm^{-2}$ doses, respectively).

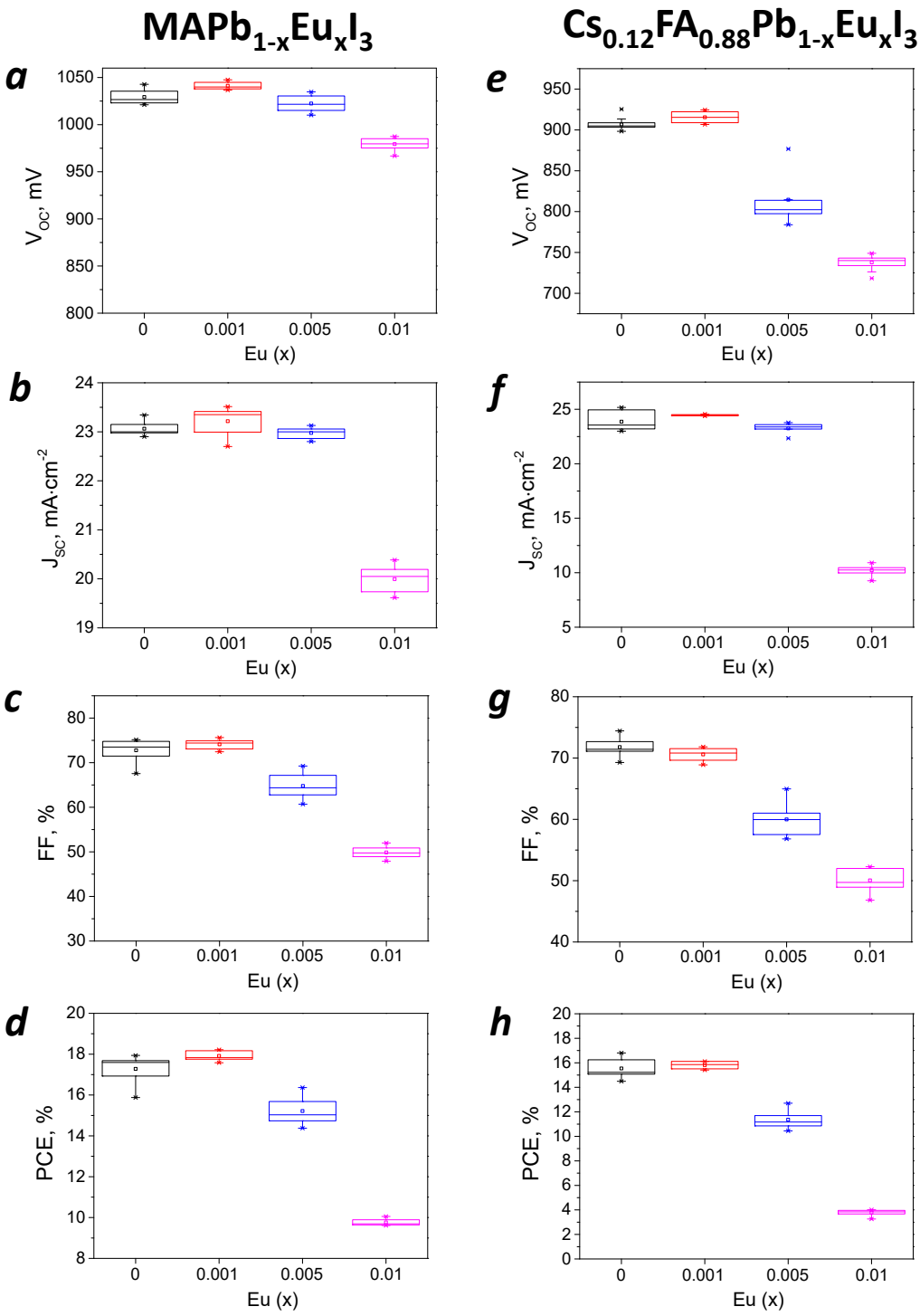

Figure S6. The influence of Eu-loading on the photovoltaic characteristics (V_{OC}, J_{SC}, FF, and PCE) of n-i-p PSCs (ITO/SnO_2/PCBA/$Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ or $MAPb_{1-x}M_xI_3$/PTA/$V_2O_{5-\delta}$/Al) based on $MAPb_{1-x}Eu_xI_3$ (a) and $Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ (b), where x = 0.001, 0.005, and 0.01.

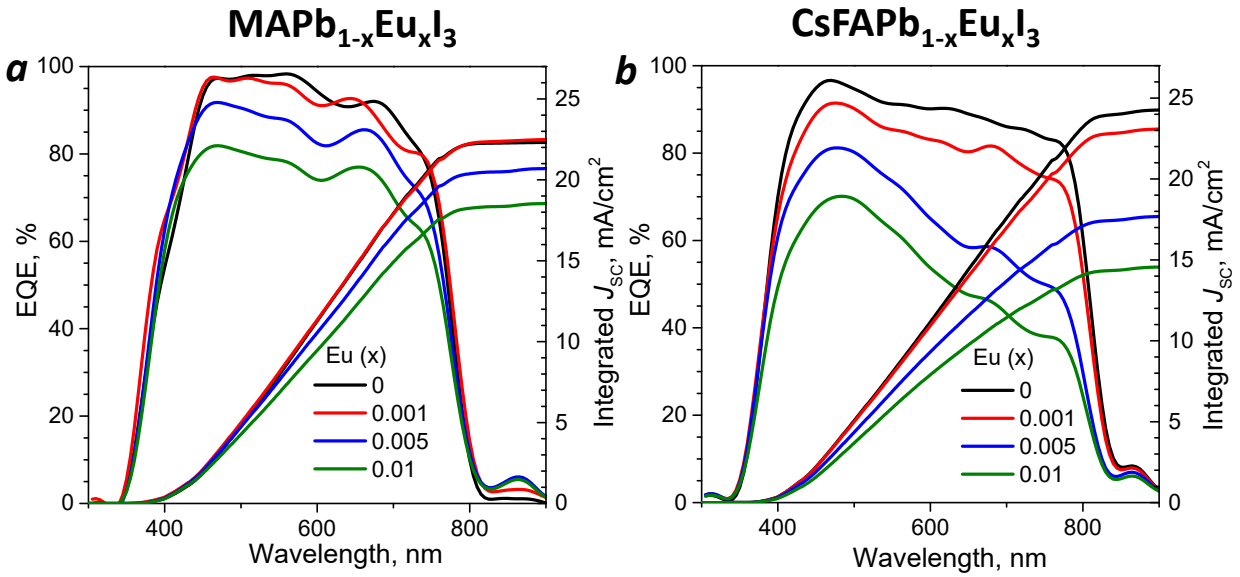

Figure S7. The EQE spectra of the solar cells with the structure of ITO/SnO_2/PCBA/perovskite/PTA/$V_2O_{5-\delta}$/Al based on the or $MAPb_{1-x}M_xI_3$ (a) and $Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ (b), where x= 0, 0.001, 0.05, and 0.01.

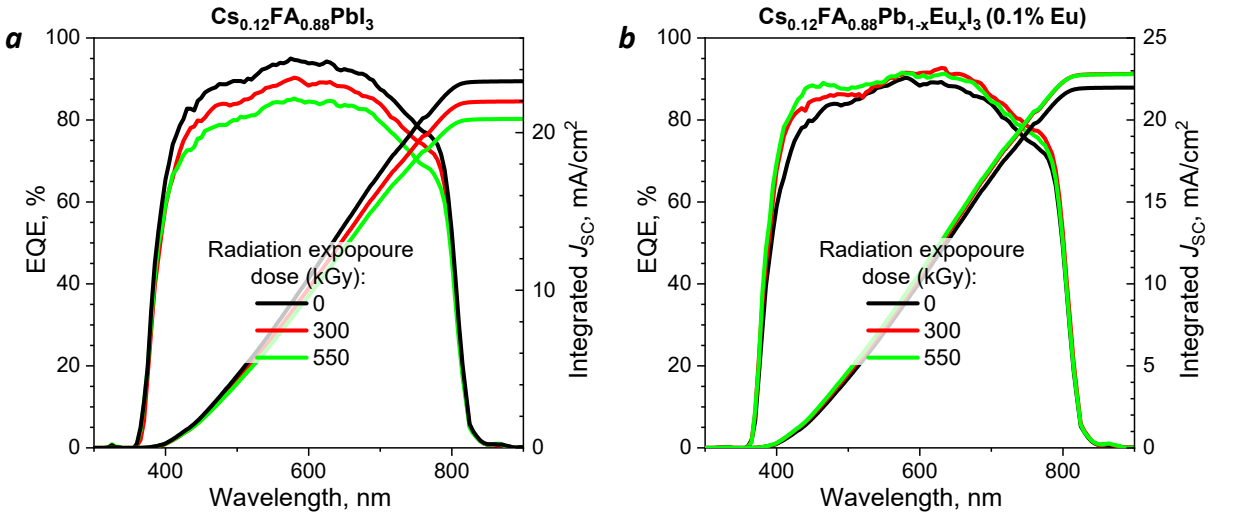

Figure S8. Evolution of the EQE spectra of the PET/ITO/PTA/Perovskite/PCBM/BCP/Al solar cells upon exposure to ^{60}Co gamma rays.

Table S1. Surface composition of the $MAPb_{1-x}Eu_xI_3$ perovskite films (in at.%).

Sample	**Si**	**C**	**O**	**N**	**N:(Pb+Eu)**	**Pb**	**I**	**I:(Pb+Eu)**	**Eu**	**Eu:Pb**
undoped	5.6	45.9	9.2	6.6	0.67	9.8	22.9	2.33	-	-
1% Eu	6.1	44.3	14.2	5	0.48	9.3	20.1	1.95	1.0	0.11
5% Eu	4.4	54.0	13.3	3.9	0.36	6.2	16.1	1.93	2.1	0.34
10% Eu	3.0	53.7	13.7	4.5	0.49	5.1	16.0	1.76	4.0	0.78

Table S2. Surface composition of the $Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ perovskite films (in at.%).

Sample	**C**	**O**	**N**	**N:(Pb+Eu)**	**Pb**	**I**	**Cs**	**I:(Pb+Eu)**	**Eu**	**Eu:Pb**
undoped	30	2.1	20.1	1,53	13.1	33.4	1.3	2.55	-	-
1% Eu	42.2	5.7	14.7	1,37	9	25.8	0.9	2.41	1.7	0.19
5% Eu	43.3	13.5	8.8	0,80	5.5	22.8	0.6	2.07	5.5	1
10% Eu	47.7	16.7	6	0,55	5.5	18	0.7	1.81	5.4	0.98
20% Eu	46.2	20.6	5.2	0,53	3.5	17.5	0.6	1.77	6.4	1.83

Table S3. The average and the best (in brackets) values of power conversion efficiency (η), open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) of the ITO/SnO_2/PCBA/$MAPb_{1-x}M_xI_3$ or $Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$/PTA/$V_2O_{5-\delta}$/Al devices (x = 0.001, 0.005 and 0.01).*

Composition	Scan	V_{OC}, V	J_{SC}, mA cm^{-2}	FF, %	PCE, %
$MAPb_{1-x}Eu_xI_3$					
x = 0 (Pristine)	Forward	(1.042) 1.029±0.009	(23.3) 23.1±0.1	(74.5) 72.0±3.1	(17.6) 17.1±0.8
	Reverse	(1.043) 1.029±0.009	(23.3) 23.0±0.2	(75.1) 73.6±2.1	(17.9) 17.5±0.6
x = 0.001	**Forward**	**(1.047) 1.041±0.004**	**(23.5) 23.3±0.3**	**(74.4) 73.3±0.8**	**(17.9) 17.7±0.2**
	Reverse	**(1.047) 1.041±0.005**	**(23.4) 23.2±0.3**	**(75.2) 75.0±0.6**	**(18.2) 18.1±0.2**
x = 0.005	Forward	(1.034) 1.024±0.008	(23.0) 22.9±0.1	(69.2) 65.7±2.3	(16.3) 15.4±0.5
	Reverse	(1.035) 1.021±0.009	(23.1) 23.0±0.1	(68.0) 63.9±2.8	(16.0) 15.0±0.7
x = 0.01	Forward	(0.987) 0.982±0.005	(20.4) 20.0±0.3	(50.2) 49.0±0.9	(9.7) 9.6±0.1
	Reverse	(0.986) 0.976±0.008	(20.2) 19.9±0.3	(52.0) 50.8±1.2	(10.1) 9.8±0.2
$Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$					
x = 0 (Pristine)	Forward	(0.905) 0.904±0.004	(24.9) 23.6±0.7	(72.7) 71.8±0.7	(16.3) 15.3±0.5
	Reverse	(0.925) 0.908±0.007	(25.2) 24.0±0.9	(74.4) 71.8±1.7	(16.8) 15.7±0.9
x = 0.001	**Forward**	**(0.911) 0.908±0.003**	**(24.6) 24.5±0.1**	**(70.4) 70.0±1.1**	**(15.6) 15.5±0.1**
	Reverse	**(0.925) 0.922±0.003**	**(24.5) 24.4±0.1**	**(71.8) 71.5±0.4**	**(16.2) 16.1±0.1**
x = 0.005	Forward	(0.877) 0.813±0.031	(23.8) 23.3±0.5	(64.4) 58.7±2.8	(12.6) 11.1±0.7
	Reverse	(0.873) 0.816±0.029	(23.7) 23.2±0.5	(65.0) 61.3±2.0	(12.7) 11.6±0.6
x = 0.01	Forward	(0.749) 0.740±0.008	(10.3) 10.0±0.4	(52.3) 51.6±0.9	(4.0) 3.8±0.3
	Reverse	(0.743) 0.735±0.009	(10.9) 10.4±0.4	(49.3) 48.5±0.9	(4.0) 3.7±0.3

* - The *J*-V curves were measured in forward and reverse directions with the scan rate of 0.01 V/s

Table S4. The average and the best (in brackets) values of power conversion efficiency (η), open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) of the PET/ITO/PTA/$Cs_{0.12}FA_{0.88}Pb_{1-x}Eu_xI_3$ (x=0 and 0.001)/PCBM/BCP/Al devices.*

Composition	**Scan direction**	**V_{OC}, V**	**J_{SC}, mA cm^{-2}**	**FF, %**	**PCE, %**
x = 0.001	Forward	(0.958) 0.950±0.022	(22.6) 22.0±0.5	(79.3) 73.7±4.3	(17.1) 15.4±1.2
	Reverse	(0.983) 0.949±0.023	(22.5) 21.8±0.8	(78.7) 75.4±2.1	(17.5) 15.6±1.3
x = 0 (Pristine)	Forward	(1.022) 0.982±0.059	(23.0) 22.4±1.1	(78.2) 71.3±7.5	(18.4) 15.7±1.8
	Reverse	(1.026) 0.978±0.060	(23.2) 22.4±1.0	(79.0) 72.5±7.3	(19.0) 15.9±2.2

* - The J-V curves were measured in forward and reverse directions with the scan rate of 0.01 V/s