Supporting Information

Interfacial engineering at the 2D/3D heterojunction for high-performance perovskite solar cells

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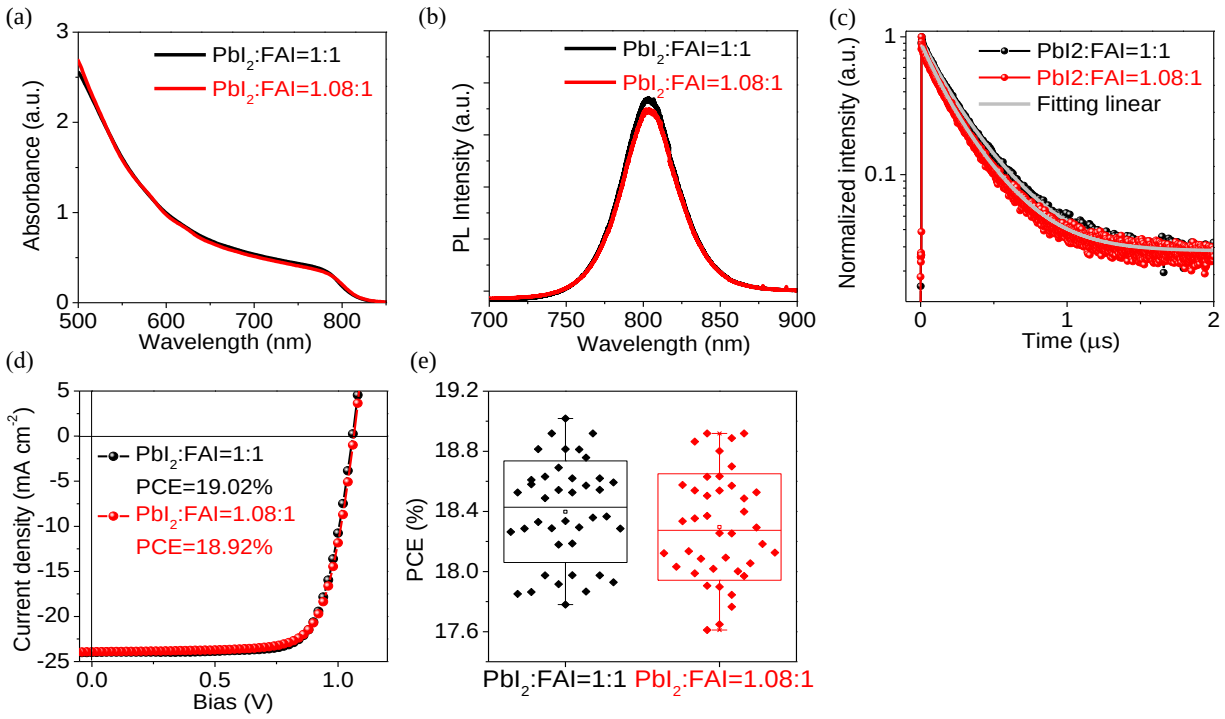

Figure S1. (a-c) Steady-state photoluminescence (PL), time-resolved PL spectroscopy (TRPL) and absorption spectra of the $FAPbI_3$ films with different molar ratio of PbI_2 and FAI. (d) J-V curves of champion devices. (e) Statistics of 40 devices for $FAPbI_3$ films with different molar ratio of PbI_2 and FAI. Negligible variations in the absorption, emission, carrier lifetime and device performance were observed despite of an extra PbI_2 was introduced, which suggests that the impact of PbI_2 passivation can be excluded.

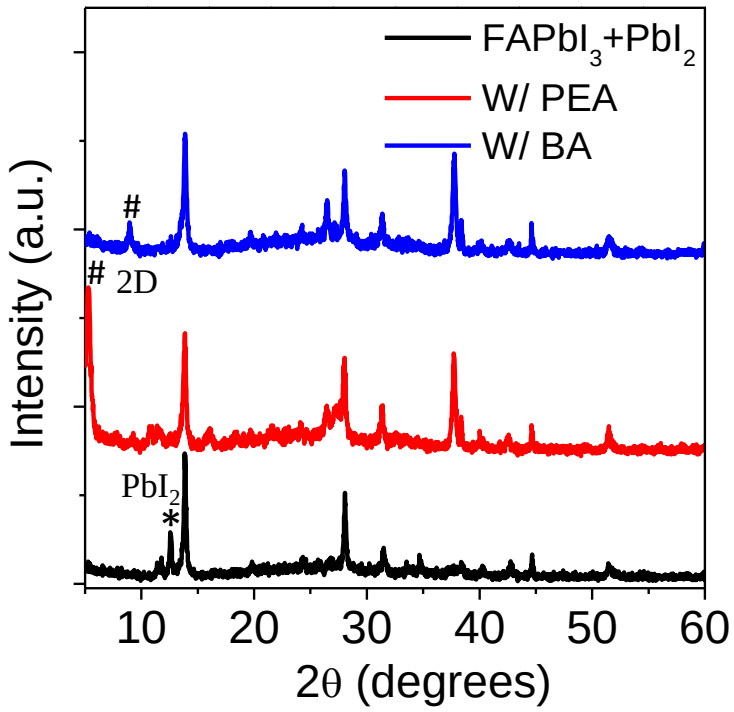

Figure S2. X-ray diffraction (XRD) patterns of the $FAPbI_3$+PbI_2 and 2D/3D films. Peaks denoted with star and pound signs originate from PbI_2 and 2D perovskite phases.

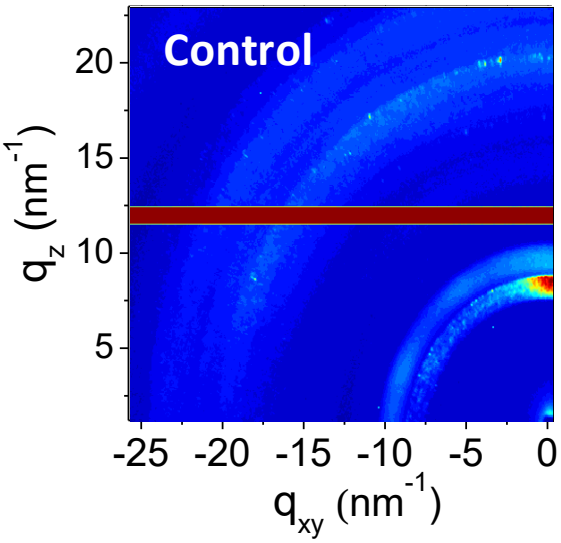

Figure S3. *Ex situ* GIWAXS pattern of the control film.

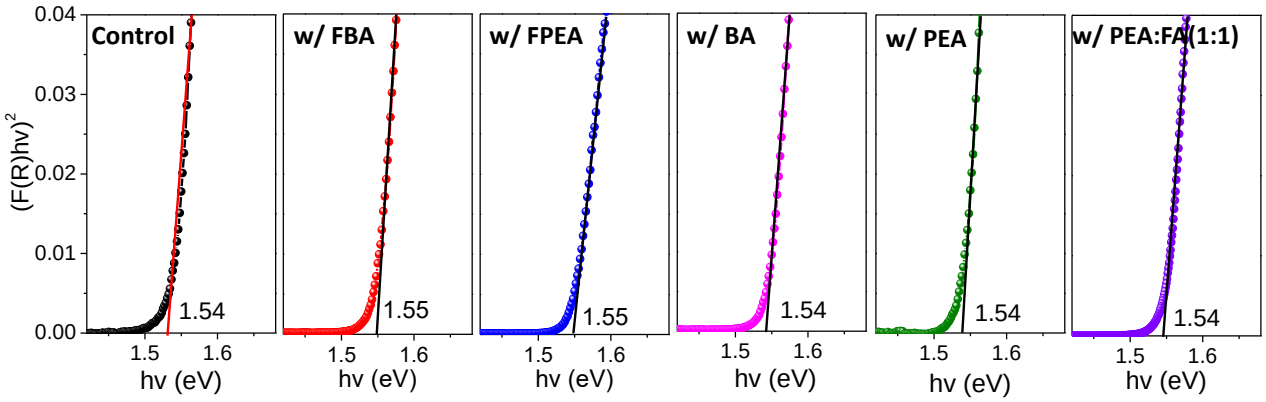

Figure S4. Tauc plots for the control, FBA-, FPEA-, BA-, PEA- and PEA:FA(1:1)-based 2D/3D perovskites determining the similar bandgap (E_g).

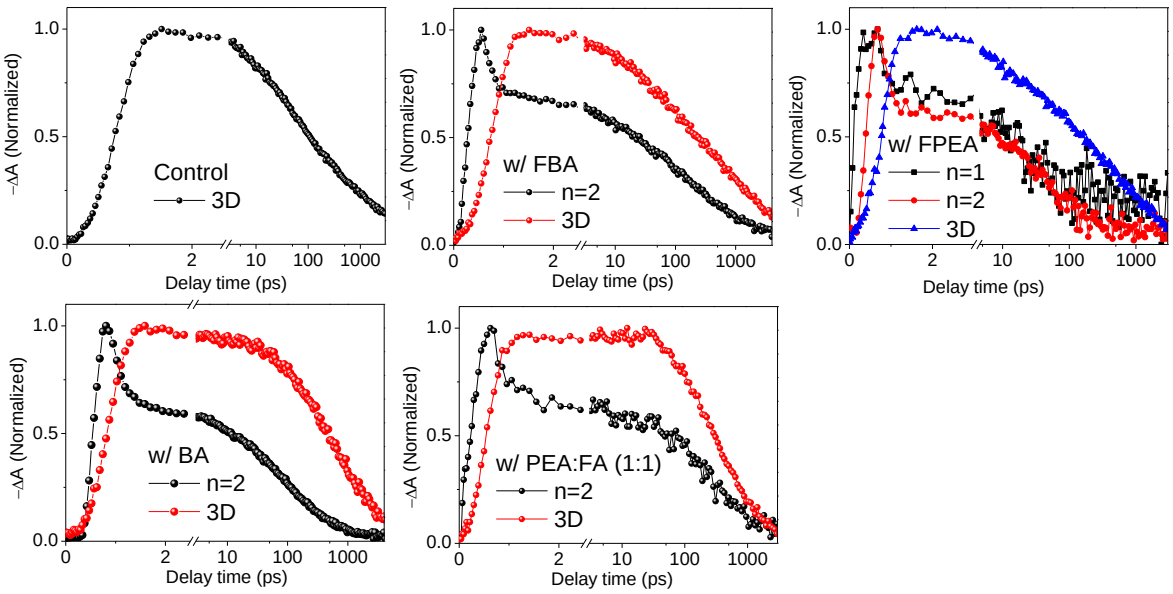

Figure S5. The dynamic evolution of the bleaching recovery for the control and 2D/3D films.

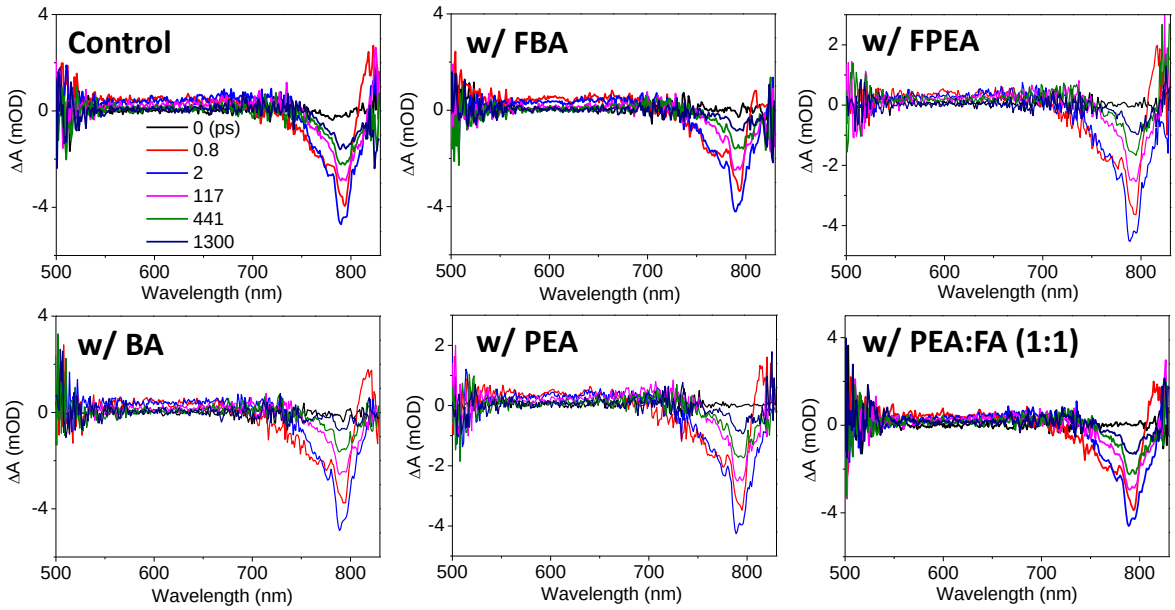

Figure S6. Transient absorption (TA) spectra at different delay times of the control and 2D/3D films under back-excitation.

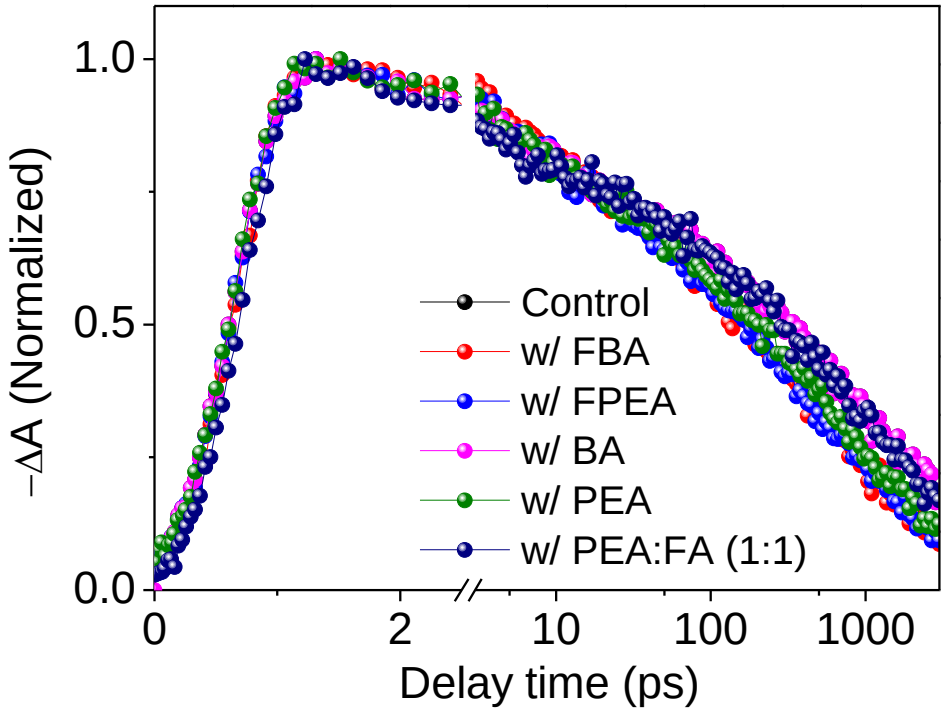

Figure S7. TA kinetics of control and 2D/3D films under back-excitation.

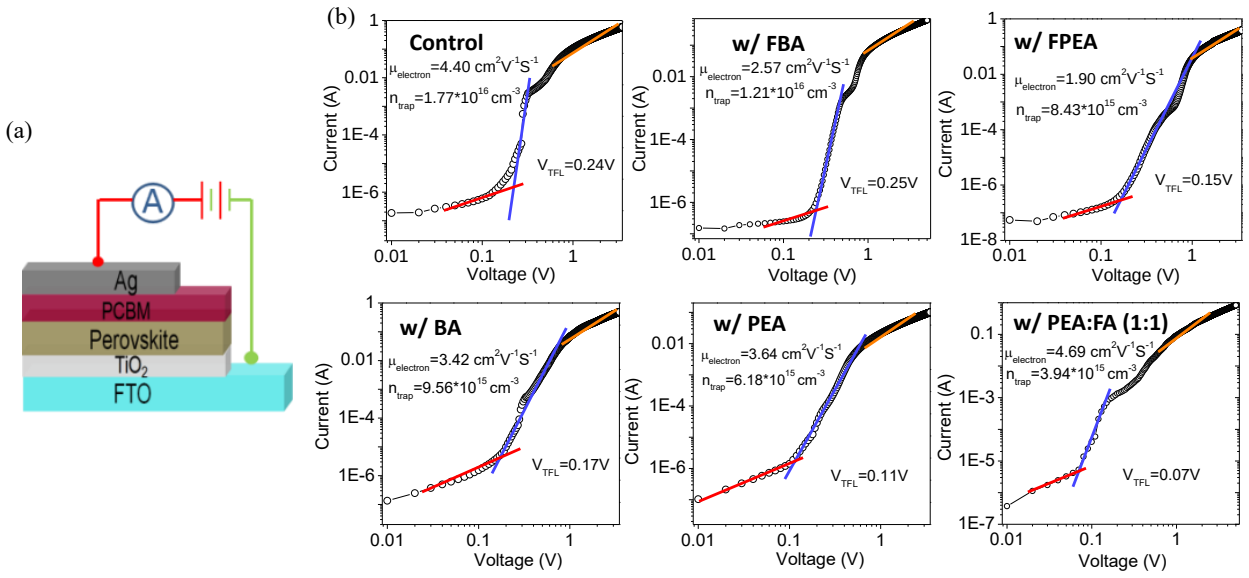

Figure S8. (a) The electron-only device structures. (b) Dark *I-V* measurement of the electron-only devices for the control and 2D/3D films with different 2D capping layers displaying V_{TFL} kink point behavior.

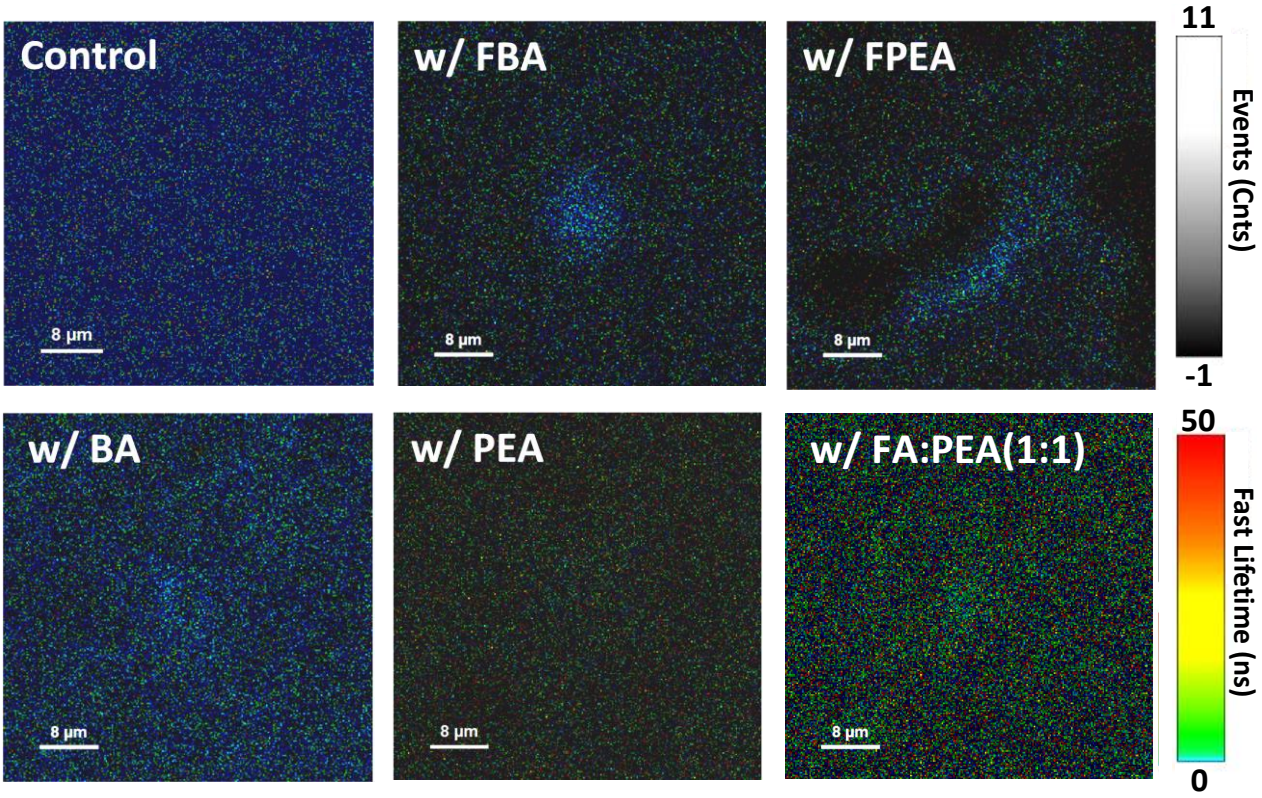

Figure S9. Overlapped intensity/lifetime PL mapping images of control and 2D/3D films (the excitation wavelength is 510 nm). The BA-, PEA- and PEA:FA(1:1)-based 2D/3D films exhibit the distinctly increased carrier lifetime accompanied with improved uniformity in contrast to the control film.

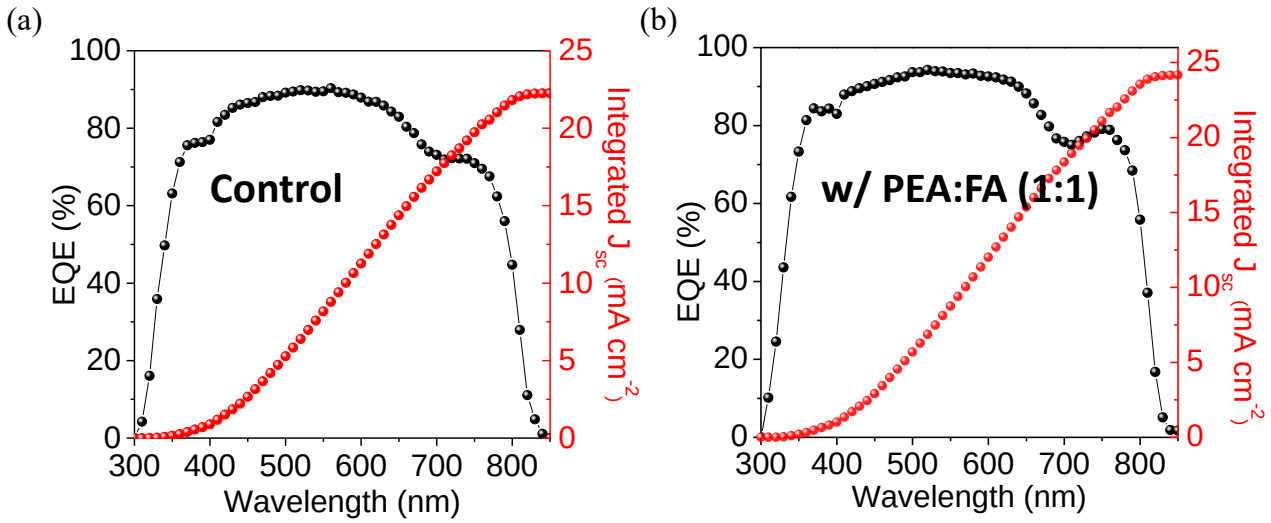

Figure S10. (a and b) External quantum efficiency (EQE) and the corresponding integrated short circuit density (J_{sc}) for the champion devices obtained for the control and PEA:FA(1:1)-based 2D/3D films.

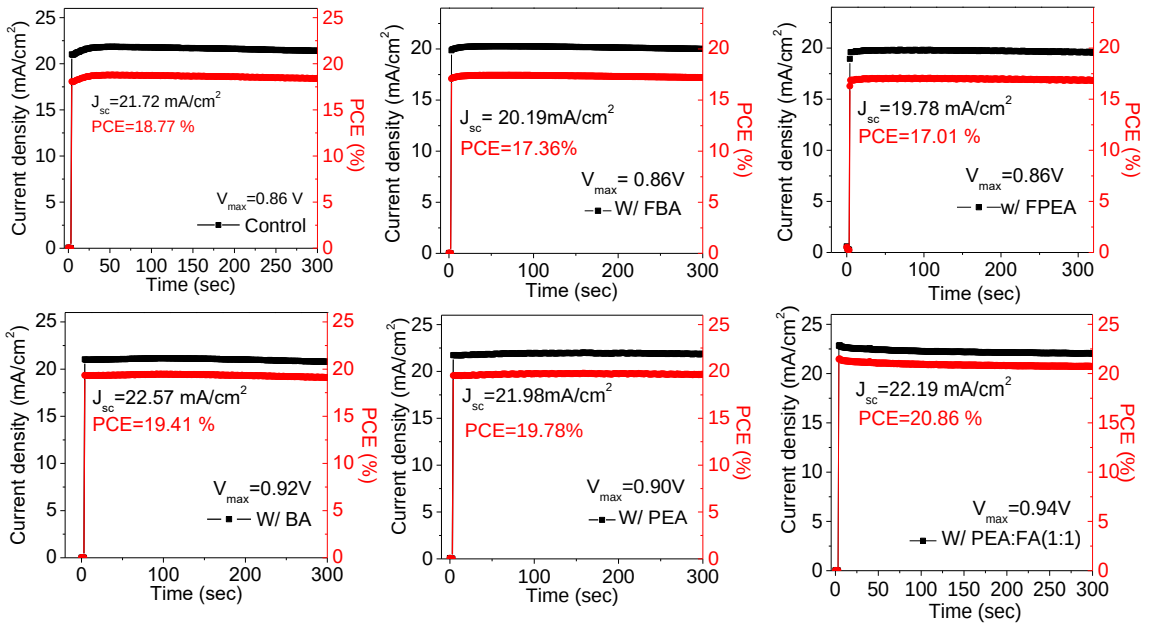

Figure S11. The stabilized power output of the champion devices for 2D/3D perovskite measured at a fixed maximum power point (MPP) voltage as a function of time.

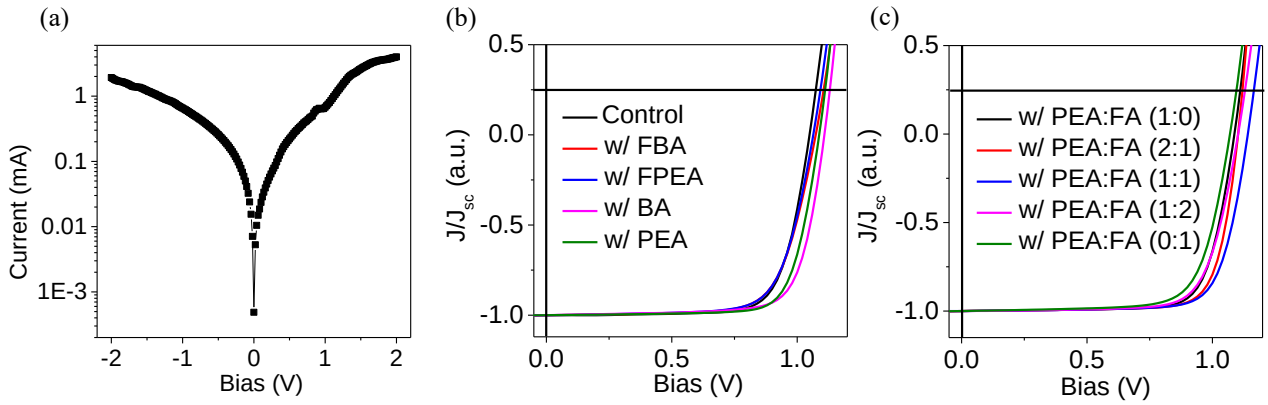

Figure S12. (a) The dark J-V curve of the representative control device. The dark curve for the control device is significantly lower than the photocurrent of the same device, suggesting that the contributions from extrinsic resistances are slight to the slopes from *J-V* curves at OC and SC. (b and c) The normalized light *J-V* curves of devices for the control and 2D/3D perovskites.

Table S1. Photovoltaic parameters of champion devices based on the control and 2D/3D films.

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Control	1.06	23.99	74.8	19.02
w/ FBA	1.07	22.63	72.0	17.51
w/ FPEA	1.06	22.13	72.8	17.14
w/ BA	1.11	23.12	76.0	19.50
w/ PEA	1.09	23.76	76.8	19.84
w/ PEA:FA(2:1)	1.10	23.50	78.3	20.28
w/ PEA:FA(1:1)	1.14	24.20	76.6	21.15
w/ PEA:FA(1:2)	1.10	23.69	74.5	19.46
w/ PEA:FA(0:1)	1.07	22.48	73.5	17.68

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	PCE_{max} (%)
Control	1.05±0.01	24.02±0.37	73.1±1.5	18.10±0.46	19.02
w/ FBA	1.05±0.02	22.57±0.31	71.5±2.1	16.95±0.40	17.51
w/ FPEA	1.05±0.01	22.19±0.23	71.8±1.0	16.64±0.65	17.14
w/ BA	1.09±0.02	23.13±0.12	74.7±0.9	18.42±0.42	19.50
w/ PEA	1.08±0.02	23.54±0.35	75.1±1.9	18.86±0.54	19.84
w/ PEA:FA(2:1)	1.07±0.02	23.46±0.32	75.0±1.2	18.71±0.51	20.28
w/ PEA:FA(1:1)	1.10±0.02	23.39±0.56	74.7±1.4	20.21±0.73	21.15
w/ PEA:FA(1:2)	1.06±0.02	23.01±0.42	71.4±1.7	17.47±0.89	19.46
w/ PEA:FA(0:1)	1.05±0.02	22.52±0.48	71.9±0.9	16.99±0.32	17.68

Table S2. Summaries of fitting parameters for time-resolved photoluminescence (TRPL) for the different films.

	Control	w/ FBA	w/ FPEA	w/ BA	w/ PEA	w/ PEA:FA(1:1)
A_1	4446.7	2793.4	6020.6	3429.6	3551.4	7182.2
τ_1 (ns)	211.5	166.8	129.4	301.6	372.1	285.8
A_2	4857.4	5155.2	4997.4	6496.5	5137.1	2163.3
τ_2 (ns)	50.1	23.3	27.5	57.3	58.9	83.0
τ_{ave} (ns)	171.9	137.3	129.4	236.9	313.8	269.5

Table S3. The hysteresis parameters of devices based on the control and 2D/3D films.

	Scanning mode	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	Hysteresis index (%)
Control	Reverse	1.06	23.99	74.8	19.02	8.9
	Forward	1.02	23.56	71.8	17.32	
w/ FBA	Reverse	1.07	22.63	72.0	17.51	2.9
	Forward	1.07	22.30	71.3	17.00	
w/ FPEA	Reverse	1.06	22.13	72.8	17.14	5.0
	Forward	1.06	21.60	70.9	16.28	
w/ BA	Reverse	1.11	23.12	76.0	19.50	5.3
	Forward	1.09	22.69	74.9	18.46	
w/ PEA	Reverse	1.09	23.76	76.8	19.84	2.1
	Forward	1.08	23.70	76.0	19.43	
w/ PEA:FA(1:1)	Reverse	1.14	24.20	76.6	21.15	2.9
	Forward	1.13	24.12	75.7	20.54	