Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Charge carrier recombination dynamics in bi-cationic perovskite solar cell

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S1. Characterization of the perovskite films

S1.1 Entropy analysis

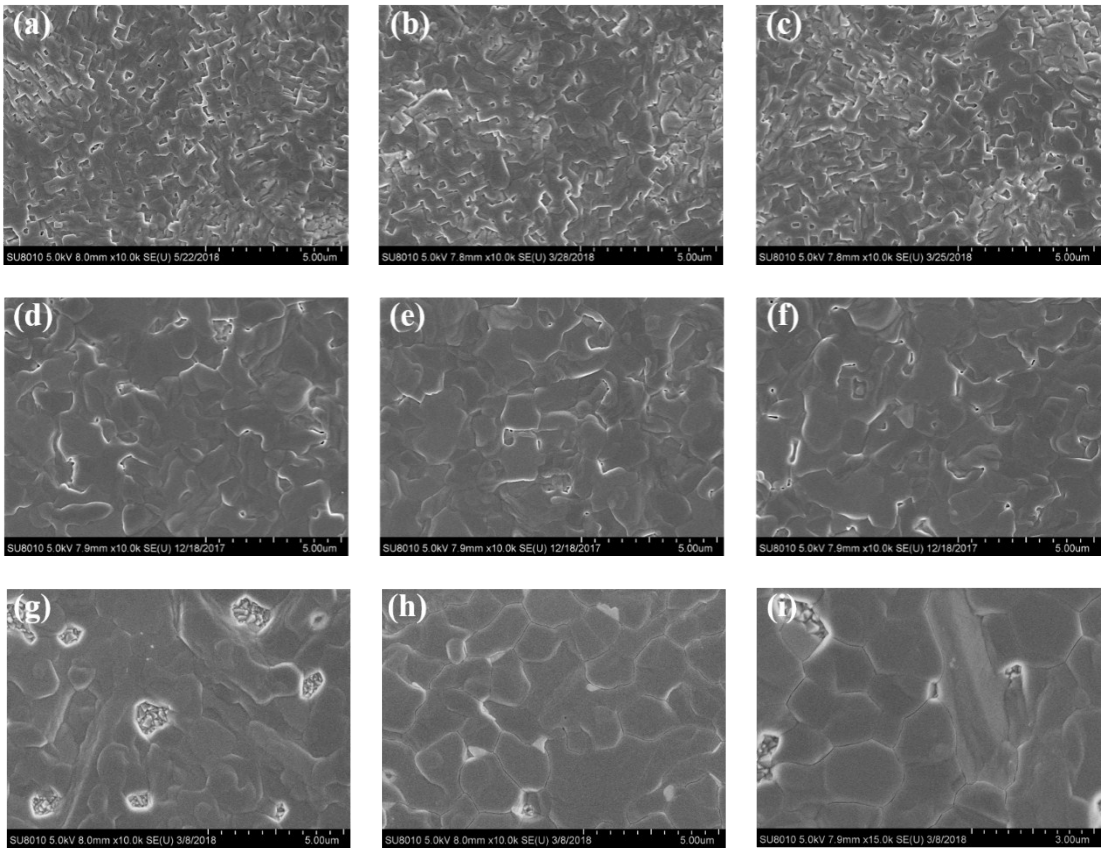

Fig. S1 SEM top views of perovskite films on c-TiO_2-coated FTO substrate ((a)-(c) MA, (d)-(f) MA+FA, (g)-(i) FA).

The irregularity of SEM images obtained from digital image analysis was used to evaluate the morphology of perovskite films. 9 sets of SEM images of perovskite films in grayscale format (524×393 pixels) were taken. By default, the entire interval was divided into 256 subintervals. Histogram counts over these subintervals were used to calculate the entropy by the following equation,

$$Entropy = -\sum_{i=0}^{L-1} p(z_i) log_2 p(z_i)$$

where z represents intensity subinterval, p is the number of pixels per intensity subinterval. The entropy was used as a statistical scalar for measuring SEM image irregularity.[1]

Table S1 Entropy of three groups of the MA, MA+FA and FA perovskite films.

Entropy	1	2	3	Mean
MA	5.54	5.57	5.60	5.57
MA+FA	4.96	4.94	4.93	4.94
FA	5.23	5.08	5.15	5.15

S1.2 X-ray diffraction

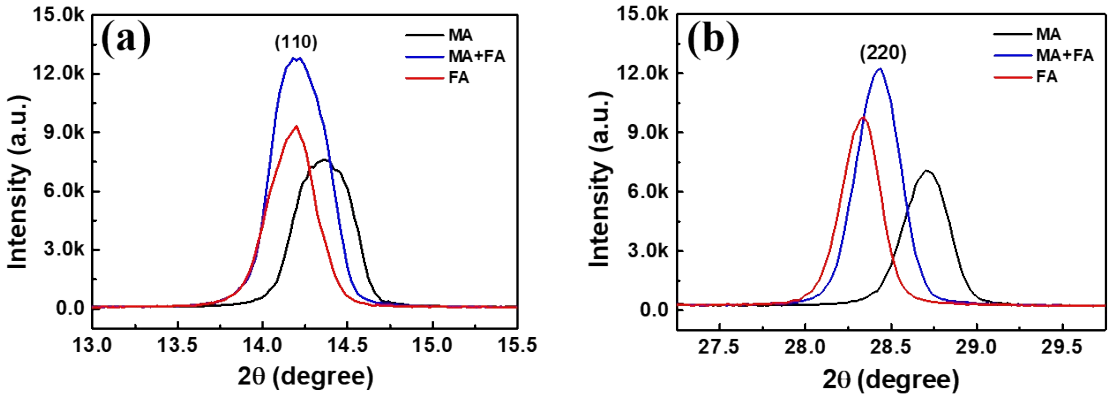

Fig. S2 (a) (110) and (b) (220) XRD peaks of MA, MA+FA and FA films.

S1.3 High-resolution transmission electron microscopy

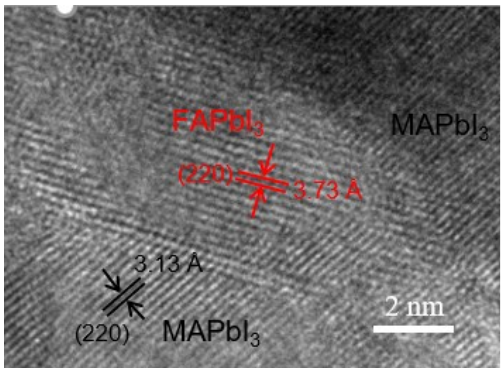

Fig. S3 HRTEM image of mixed MA+FA perovskite sample.

S2. Device characterization

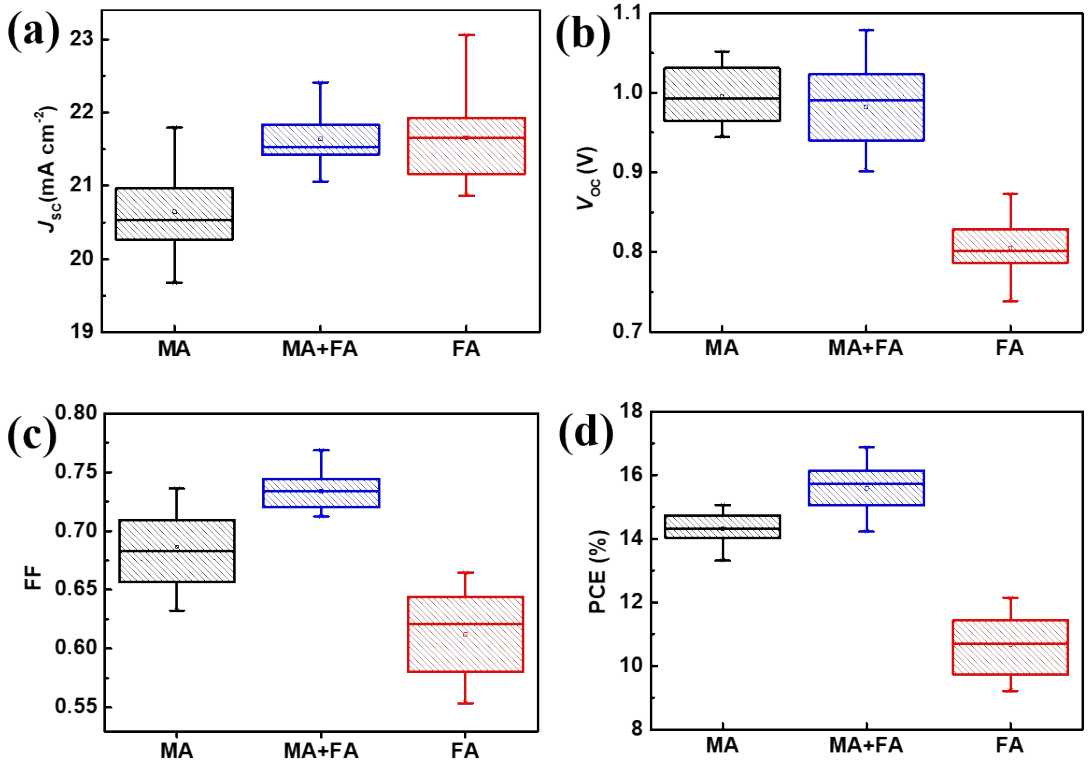

Fig. S4 Statistical parameters of (a) J_{SC}, (b) V_{OC}, (c) FF and (d) PCE for MA (black), MA+FA (blue) and FA (red) devices under reverse scan. Statistical measurements of thirty samples were performed for the three devices, respectively.

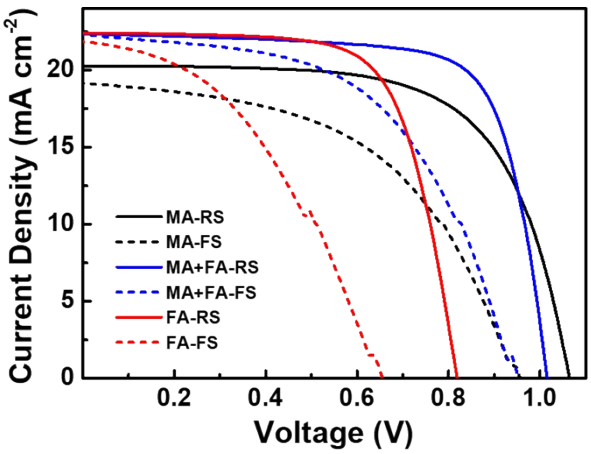

Fig. S5 *J-V* curves of MA, MA+FA and FA devices measured under reverse scan (RS) and forward scan (FS).

Table S2 Photovoltaic parameters of a batch of cells measured under AM 1.5G irradiation.

	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)
MA-RS	20.25	1.06	0.63	13.49
MA-FS	19.16	0.96	0.51	9.31
MA+FA-RS	22.36	1.02	0.74	16.76
MA+FA-FS	22.30	0.95	0.54	11.47
FA-RS	22.41	0.82	0.65	11.97
FA-FS	21.86	0.66	0.42	5.99

S3. Photovoltage decay traces

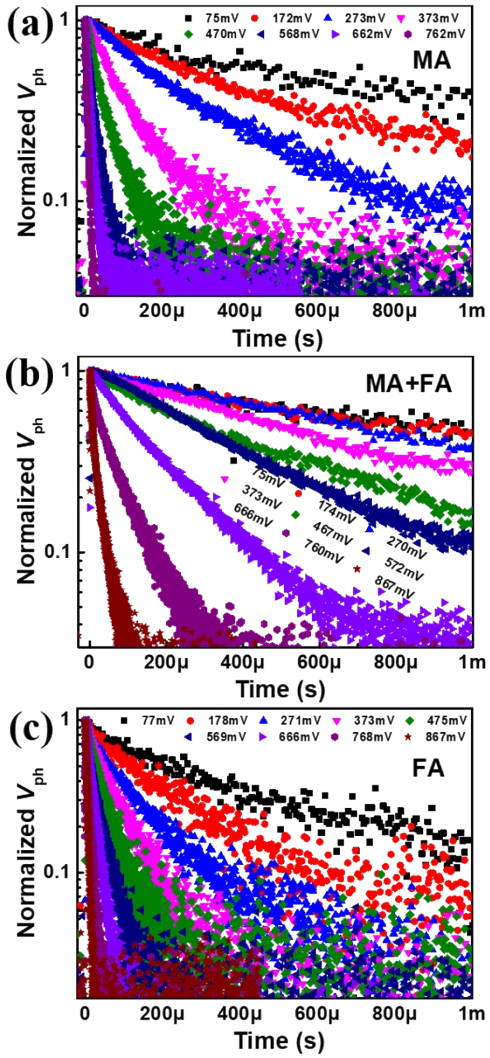

Fig. S6 The normalized TPV decay traces of diverse steady-state photovoltages of three kinds of devices of (a) MA, (b) MA+FA and (c) FA, respectively.

S3.1 The fitting of TPV

The raw TPV data were fitted with bi-exponential decay equation,

$$V_{ph}(t) = V_{base} + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where V_{base} is the baseline, A_1 and A_2 are pre-exponential factors, and τ_1 and τ_2 are time constants. The average charge recombination time constants (τ_r) were calculated as shown below,

$$\tau_r = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$$

Table S3 Parameters of bi-exponential fitting for TPV decay traces of MA device.

V_{ph} (V)	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_r (s)
0.024	0.001	0.524	9.22E-04	0.199	1.07E-02	3.62E-03
0.050	0.004	0.600	7.36E-04	0.229	9.43E-03	3.14E-03
0.075	0.004	0.224	7.23E-04	0.642	8.77E-03	2.80E-03
0.101	0.005	0.228	8.51E-04	0.657	8.67E-03	2.86E-03
0.123	0.003	0.733	5.39E-04	0.214	5.94E-03	1.76E-03
0.147	0.003	0.723	4.59E-04	0.174	4.93E-03	1.33E-03
0.172	0.006	0.186	3.56E-04	0.767	3.43E-03	9.56E-04
0.198	0.004	0.827	4.61E-04	0.167	3.93E-03	1.05E-03
0.223	0.006	0.139	2.80E-04	0.863	2.88E-03	6.42E-04
0.248	0.008	0.857	2.57E-04	0.161	1.91E-03	5.19E-04
0.273	0.006	0.127	2.19E-04	0.883	1.79E-03	4.17E-04
0.297	0.004	0.113	1.57E-04	0.897	1.45E-03	3.02E-04
0.317	0.004	0.878	1.07E-04	0.115	8.65E-04	1.95E-04
0.345	0.013	0.859	1.00E-04	0.127	5.91E-04	1.63E-04
0.373	0.008	0.917	8.74E-05	0.103	5.96E-04	1.39E-04
0.397	0.007	0.125	6.99E-05	0.918	4.35E-04	1.14E-04
0.424	0.007	0.221	5.48E-05	0.849	2.29E-04	9.07E-05

0.446	0.002	0.063	5.00E-05	0.966	4.08E-04	7.19E-05
0.470	0.006	0.915	3.25E-05	0.182	1.73E-04	5.58E-05
0.497	0.007	0.115	3.11E-05	1.003	2.20E-04	5.05E-05
0.518	0.000	0.205	2.23E-05	0.940	9.43E-05	3.52E-05
0.544	0.003	0.130	2.01E-05	0.985	9.61E-05	2.90E-05
0.568	0.003	0.136	1.66E-05	0.995	7.21E-05	2.33E-05
0.594	0.002	0.989	1.32E-05	0.151	6.01E-05	1.95E-05
0.614	0.002	0.989	1.09E-05	0.159	4.57E-05	1.58E-05
0.645	0.003	0.026	1.17E-05	1.104	3.36E-04	1.91E-05
0.662	0.002	1.040	9.97E-06	0.037	3.21E-04	2.07E-05
0.684	0.001	0.131	7.17E-06	1.041	2.82E-05	9.52E-06
0.710	0.003	1.042	5.77E-06	0.126	2.14E-05	7.46E-06
0.741	0.002	0.033	5.67E-06	0.961	3.14E-05	6.53E-06
0.762	0.001	0.032	5.26E-06	1.120	3.02E-05	5.95E-06
0.783	0.000	0.121	3.67E-06	0.965	1.11E-05	4.50E-06

Table S4 Parameters of bi-exponential fitting for TPV decay traces of MA+FA device.

V_{ph} (V)	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_r (s)
0.032	0.001	0.640	1.46E-03	0.263	2.58E-02	8.53E-03
0.051	0.004	0.227	1.29E-03	0.643	2.29E-02	6.94E-03
0.075	0.004	0.656	1.13E-03	0.223	2.10E-02	6.17E-03
0.101	0.007	0.218	1.08E-03	0.660	1.84E-02	5.39E-03
0.126	0.003	0.227	1.13E-03	0.701	1.92E-02	5.56E-03
0.152	0.006	0.224	1.10E-03	0.697	1.72E-02	5.02E-03
0.174	0.005	0.197	9.57E-04	0.733	1.56E-02	4.06E-03
0.197	0.005	0.733	1.28E-03	0.246	1.55E-02	4.86E-03
0.224	0.004	0.241	1.12E-03	0.761	1.42E-02	4.27E-03
0.249	0.004	0.294	1.46E-03	0.720	1.51E-02	5.42E-03
0.270	0.003	0.158	7.98E-04	0.834	1.08E-02	2.40E-03

0.296	0.003	0.150	6.40E-04	0.791	9.84E-03	2.11E-03
0.319	0.007	0.816	5.99E-04	0.164	7.10E-03	1.69E-03
0.346	0.003	0.155	5.83E-04	0.797	7.04E-03	1.64E-03
0.373	0.004	0.820	5.73E-04	0.161	6.54E-03	1.55E-03
0.391	0.005	0.141	4.69E-04	0.830	5.41E-03	1.19E-03
0.416	0.005	0.816	4.42E-04	0.134	4.86E-03	1.06E-03
0.445	0.010	0.156	4.27E-04	0.827	3.51E-03	9.14E-04
0.467	0.003	0.828	4.00E-04	0.118	4.18E-03	8.71E-04
0.496	0.002	0.888	4.18E-04	0.106	4.54E-03	8.59E-04
0.517	0.003	0.116	3.15E-04	0.853	2.72E-03	6.03E-04
0.544	0.000	0.921	3.23E-04	0.097	3.07E-03	5.84E-04
0.572	-0.003	0.969	3.35E-04	0.082	3.48E-03	5.80E-04
0.588	0.000	0.854	2.29E-04	0.087	2.14E-03	4.05E-04
0.619	-0.001	0.069	2.01E-04	0.896	1.78E-03	3.14E-04
0.642	0.005	0.868	1.69E-04	0.113	7.89E-04	2.40E-04
0.666	0.003	0.933	1.55E-04	0.059	1.04E-03	2.08E-04
0.690	0.003	0.278	9.15E-05	0.711	2.98E-04	1.49E-04
0.720	0.001	0.216	8.32E-05	0.807	2.67E-04	1.22E-04
0.737	0.005	0.413	2.83E-05	0.581	1.27E-04	8.63E-05
0.760	0.002	0.550	1.97E-05	0.401	9.82E-05	6.51E-05
0.784	0.001	0.455	1.48E-05	0.530	7.96E-05	4.97E-05
0.811	0.001	0.570	1.09E-05	0.462	5.89E-05	3.74E-05
0.841	0.002	0.480	7.04E-06	0.557	4.10E-05	2.28E-05
0.867	0.002	0.421	5.26E-06	0.584	3.23E-05	1.66E-05
0.889	0.002	0.450	4.49E-06	0.271	2.53E-05	1.23E-05

Table S5 Parameters of bi-exponential fitting for TPV decay traces of FA device.

V_{ph} (V)	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_r (s)
0.025	-0.007	0.406	2.85E-04	0.453	1.33E-03	7.80E-04

0.051	-0.012	0.390	1.49E-04	0.542	9.93E-04	6.39E-04
0.077	-0.009	0.491	1.92E-04	0.444	9.01E-04	5.29E-04
0.102	-0.018	0.447	1.27E-04	0.460	6.84E-04	4.02E-04
0.125	-0.018	0.613	2.09E-04	0.289	8.03E-04	3.99E-04
0.151	-0.016	0.470	1.24E-04	0.451	5.32E-04	3.32E-04
0.178	-0.013	0.683	1.60E-04	0.233	6.21E-04	2.77E-04
0.203	-0.023	0.671	7.36E-05	0.321	3.24E-04	2.43E-04
0.226	-0.018	0.518	8.21E-05	0.434	3.29E-04	1.94E-04
0.253	-0.017	0.105	1.39E-04	0.795	5.40E-04	1.86E-04
0.271	-0.014	0.367	6.73E-05	0.567	2.85E-04	1.53E-04
0.304	-0.016	0.054	1.25E-04	0.885	7.91E-04	1.64E-04
0.324	-0.011	0.266	5.99E-05	0.703	2.66E-04	1.16E-04
0.353	-0.009	0.718	2.48E-05	0.302	1.25E-04	9.56E-05
0.373	-0.017	0.526	3.56E-05	0.466	1.23E-04	8.18E-05
0.398	-0.016	0.755	4.70E-05	0.248	1.94E-04	8.34E-05
0.424	-0.014	0.475	3.08E-05	0.543	9.89E-05	6.71E-05
0.450	-0.013	0.712	3.73E-05	0.344	1.15E-04	6.25E-05
0.475	-0.027	0.686	3.03E-05	0.340	9.80E-05	5.28E-05
0.496	-0.022	0.605	1.88E-05	0.445	7.42E-05	4.23E-05
0.525	-0.026	0.196	3.55E-05	0.900	1.05E-04	4.80E-05
0.544	-0.019	0.442	1.90E-05	0.638	6.15E-05	3.64E-05
0.569	-0.016	0.643	1.44E-05	0.452	5.18E-05	2.98E-05
0.596	-0.031	0.404	1.65E-05	0.684	4.90E-05	2.86E-05
0.620	-0.029	0.351	1.77E-05	0.761	4.54E-05	2.65E-05
0.647	-0.029	0.924	1.95E-05	0.239	4.83E-05	2.54E-05
0.666	-0.021	0.536	9.67E-06	0.608	2.95E-05	1.90E-05
0.692	-0.018	0.624	6.99E-06	0.539	2.30E-05	1.56E-05
0.718	-0.028	0.492	5.37E-06	0.636	1.87E-05	1.29E-05
0.741	-0.024	0.636	4.85E-06	0.530	1.61E-05	1.10E-05

0.768	-0.020	0.669	3.80E-06	0.512	1.30E-05	9.00E-06
0.792	-0.019	0.564	3.99E-06	0.650	1.18E-05	8.18E-06
0.824	-0.015	0.814	3.27E-06	0.476	8.41E-06	6.51E-06
0.839	-0.012	0.510	3.09E-06	0.641	7.59E-06	5.60E-06
0.867	-0.011	0.857	2.02E-06	0.491	5.76E-06	4.40E-06
0.893	-0.008	0.604	3.75E-06	0.604	3.75E-06	3.75E-06

Reference

1. X. C. Liu, H. H. Du, L. M. Fu, R. M. Han, P. Wang, X. C. Ai, J. P. Zhang and L. H. Skibsted, *Anal. Chem.*, 2018, **90**, 2126-2133.