Supporting Information

Electron Beam Irradiation of Lead Halide Perovskite Solar Cells: Dedoping of Organic Hole Transport Material Despite Hardness of the Perovskite Layer

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This supporting information presents the following contents.

Supporting Figure S1–S16

Supporting Table S1–S3

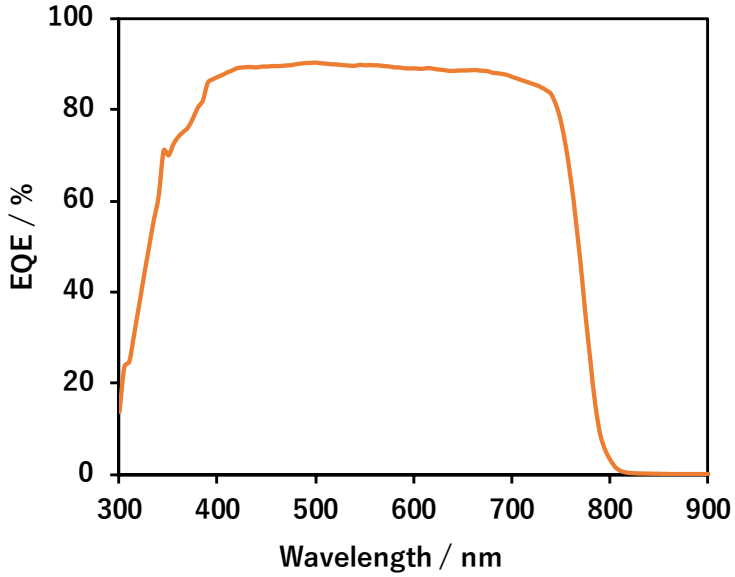

Figure S1. EQE spectrum of PSC (FTO/cTiO$_2$/mpTiO$_2$/MA$_{0.13}$FA$_{0.87}$PbI$_{2.61}$Br$_{0.39}$/doped SpiroOMeTAD/Au). The integrated J_{SC} is 22.06 mA cm^{-2} (maximum EQE: 0.90 at ~500 nm; onset: ~815 nm).

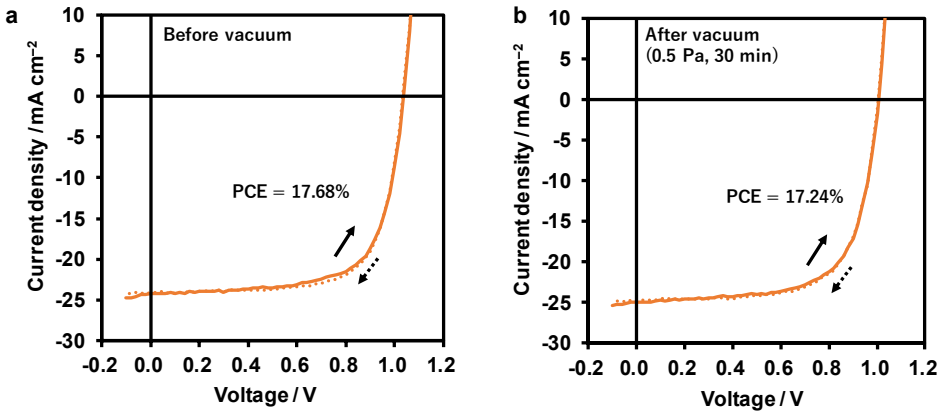

Figure S2. Best-performing *JV* curves of PSC (FTO/cTiO$_2$/mpTiO$_2$/MA$_{0.13}$FA$_{0.87}$PbI$_{2.61}$Br$_{0.39}$/ doped SpiroOMeTAD/Au) (a) before and (b) after keeping the devices in vacuum (0.5 Pa) for 30 min similar to the EB exposure condition. Note that EB is not exposed.

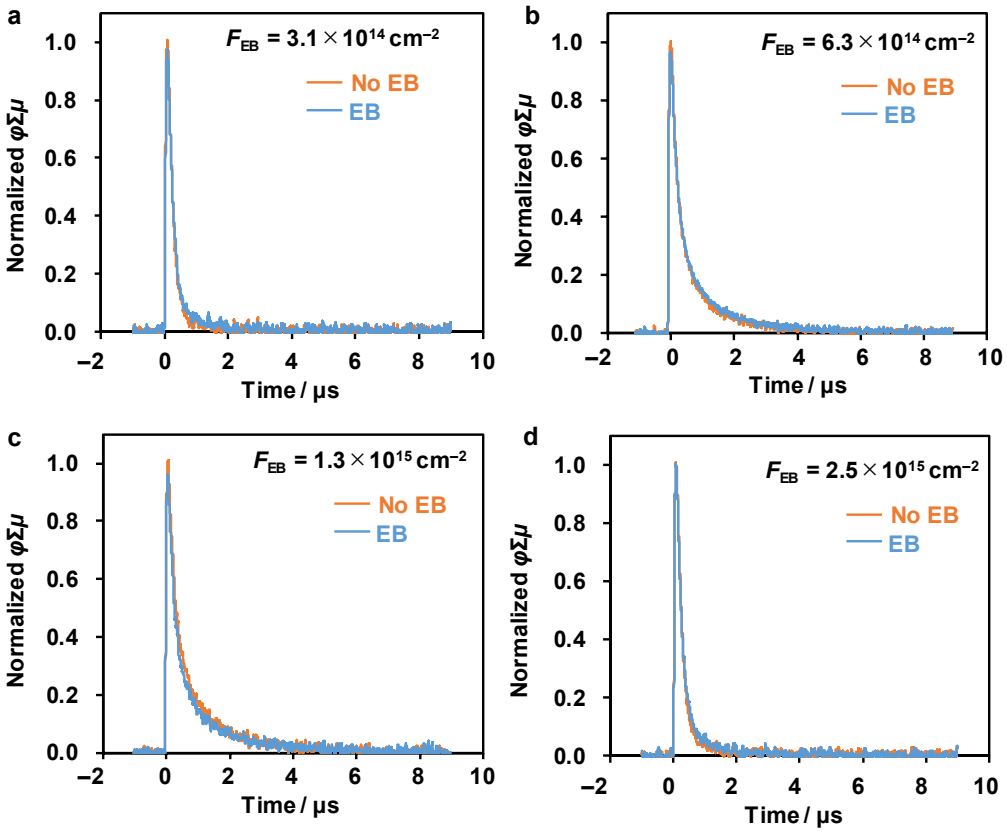

Figure S3. TRMC transients of $MA_{0.13}FA_{0.87}PbI_{2.61}Br_{0.39}$ (λ_{ex} = 500 nm) without (the orange curve) and with 100 keV EB exposure (the blue curve). They are normalized by the $\varphi\Sigma\mu_{max}$ without EB exposure. The total flurences (F_{EB}) are (a) 3.1 × 10^{14} cm^{-2}, (b) 6.3 × 10^{14} cm^{-2}, (c) 1.3 × 10^{15} cm^{-2}, and (d) 2.5 × 10^{15} cm^{-2}.

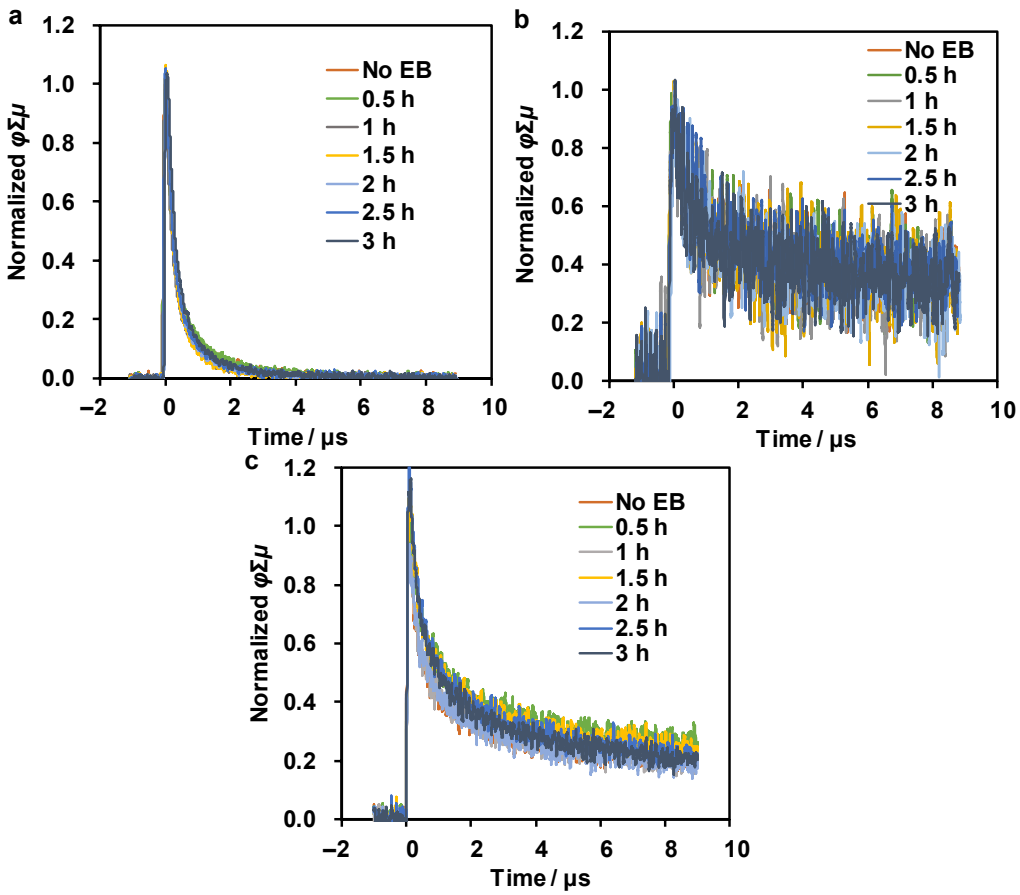

Figure S4. TRMC transients of (a) $MA_{0.13}FA_{0.87}PbI_{2.61}Br_{0.39}$ (λ_{ex} = 500 nm), (b) doped SpiroOMeTAD (λ_{ex} = 355 nm), and (c) $mpTiO_2$ (λ_{ex} = 355 nm) normalized by the $\varphi\Sigma\mu_{max}$ (the orange curve) without 100 keV EB exposure at 2.5×10^{15} cm^{-2}. Each line is the TRMC decay measured after the EB exposure (0.5 to 3 h).

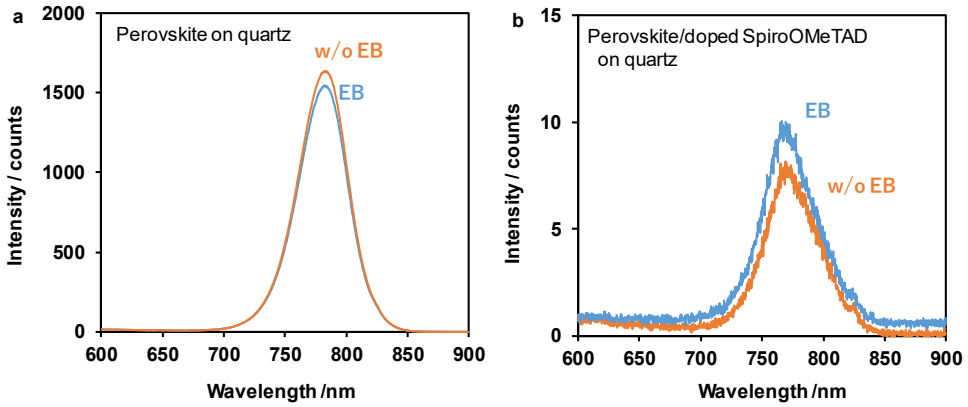

Figure S5. Photoluminescence (PL) spectra of (a) $MA_{0.13}FA_{0.87}PbI_{2.61}Br_{0.39}$ with (blue line) and without (orange line) EB exposure (100 keV at 2.5×10^{15} cm^{-2}) and (b) the perovskite/ doped SpiroOMeTAD with/without EB exposure. All of the PL spectra were measured under the same condition (slit width, etc, λ_{ex} = 400 nm).

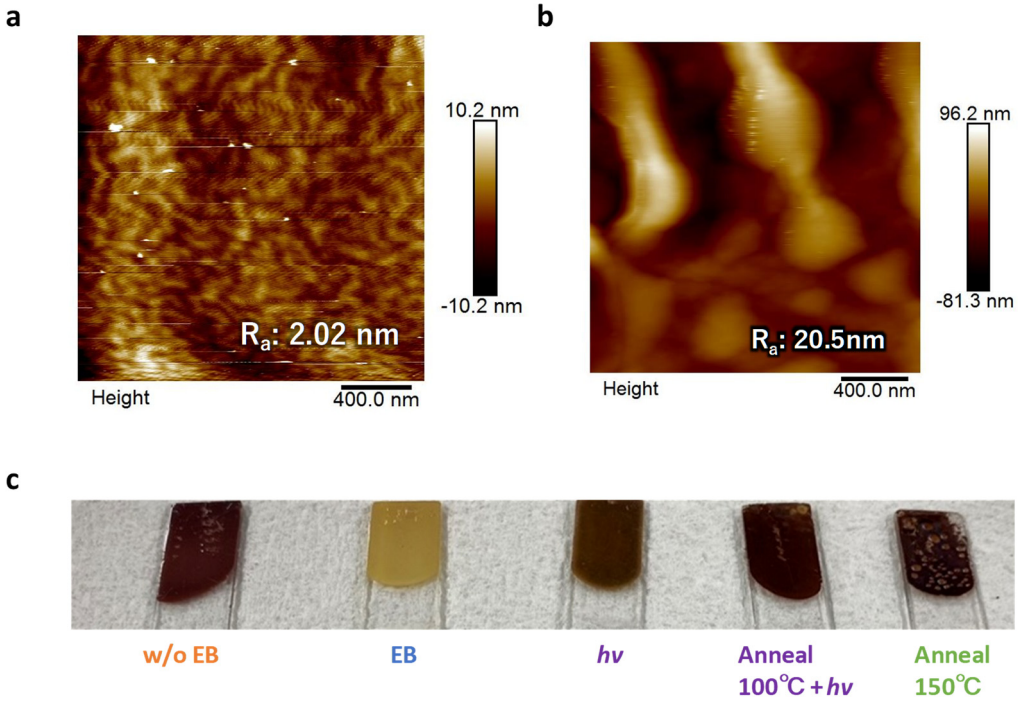

Figure S6. (a) AFM height image of the doped SpiroOMeTAD film after thermal annealing at 100 ℃ for 20 min with AM1.5G exposure. (b) AFM height image of the doped SpiroOMeTAD film after thermal annealing at 150 ℃ for 20 min. The roughness value is appended. (c) Pictures of doped SpiroOMeTAD films. From the left to the right, without EB exposure, EB (100 keV, 2.5×10^{15} cm^{-2}), the AM1.5G exposure for 20 min, thermal anneaing at 100 ℃ with AM1.5G exposure, and thermal anneaing at 150 ℃ with AM1.5G exposure. All of the films except for w/o EB were exposed to EB.

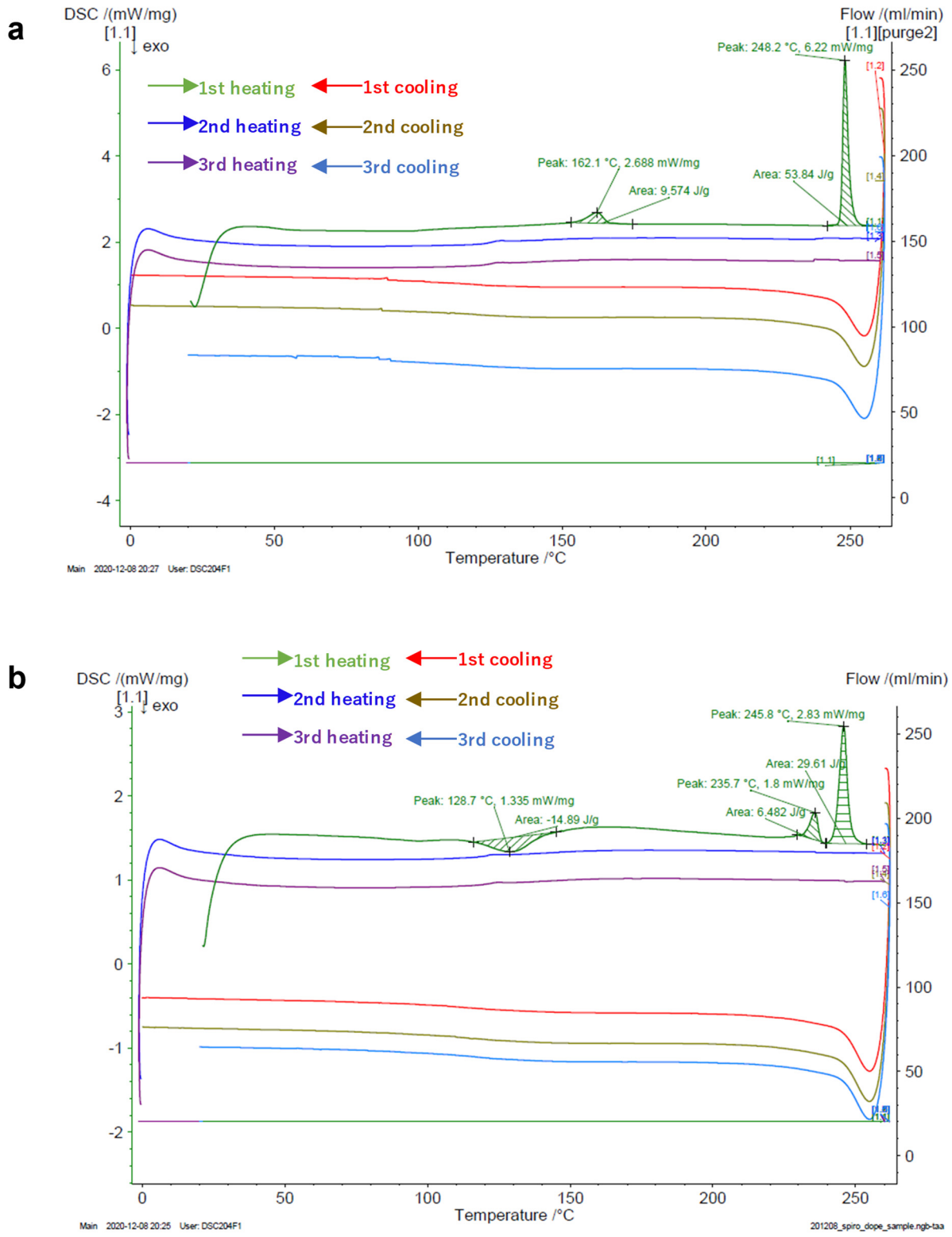

Figure S7. DSC charts of (a) SpiroOMeTAD and (b) doped SpiroOMeTAD.

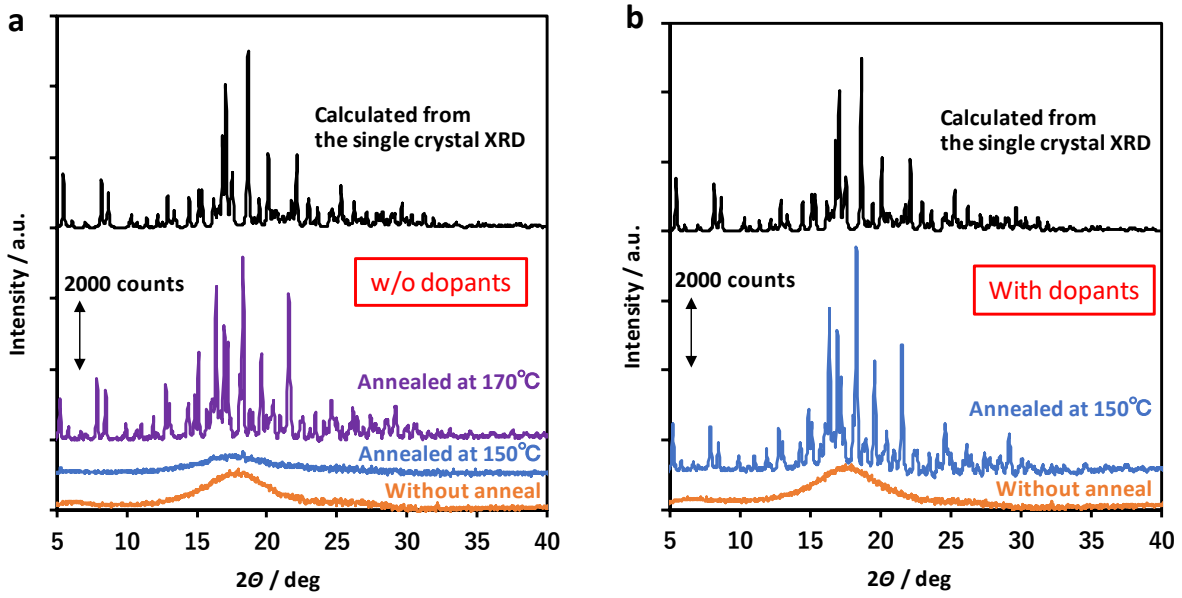

Figure S8. XRD profiles of (a) SpiroOMeTAD and (b) doped SpiroOMeTAD. The background (a broad diffraction ascribed to a quartz substrate) was subtracted. The black line is calculated from the single crystal XRD data in the literature (Shi, D.; Qin, X.; Li, Y.; He, Y.; Zhong, C.; Pan, J.; Dong, H.; Xu, W.; Li, T.; Hu, W.; Brédas, J. –L.; Bakr, O. M. Spiro-OMeTAD Single Crystals: Remarkably Enhanced Charge-Carrier Transport via Mesoscale Ordering. *Sci. Adv.* **2016**, *2*, e1501491.).

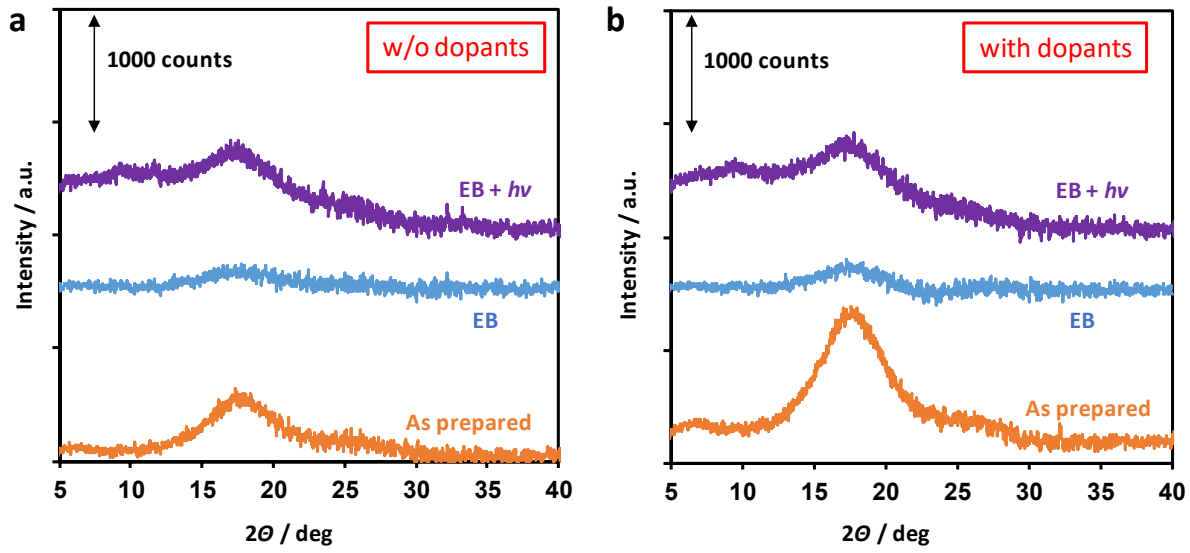

Figure S9. XRD profiles of (a) SpiroOMeTAD and (b) doped SpiroOMeTAD. The background (a broad diffraction ascribed to a quartz substrate) was subtracted. The orange, blue, and purple lines are as prepared, EB (100 keV, 2.5×10^{15} cm^{-2})-exposed, and the light (AM1.5G, 100 mW cm^{-2} for 20 min)-treated after the EB films, respectively.

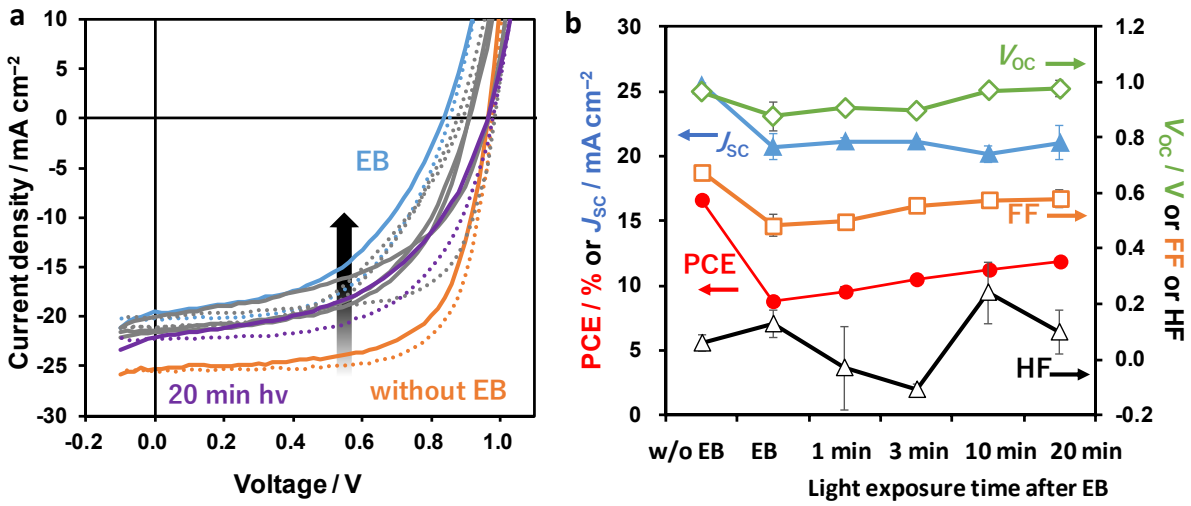

Figure S10. (a) *JV* curves of PSC devices without EB (orange line), after 100 keV 2.5×10^{15} cm^{-2} EB exposure (blue line), AM1.5G 100 mW cm^{-2} light exposure (gray lines), and after 20 min light exposure (purple line). The solid and dotted lines are forward and reverse scans, respectively. (b) PCE, J_{SC}, V_{OC}, FF, and hysteresis factor (HF) without EB, EB, and light exposure.

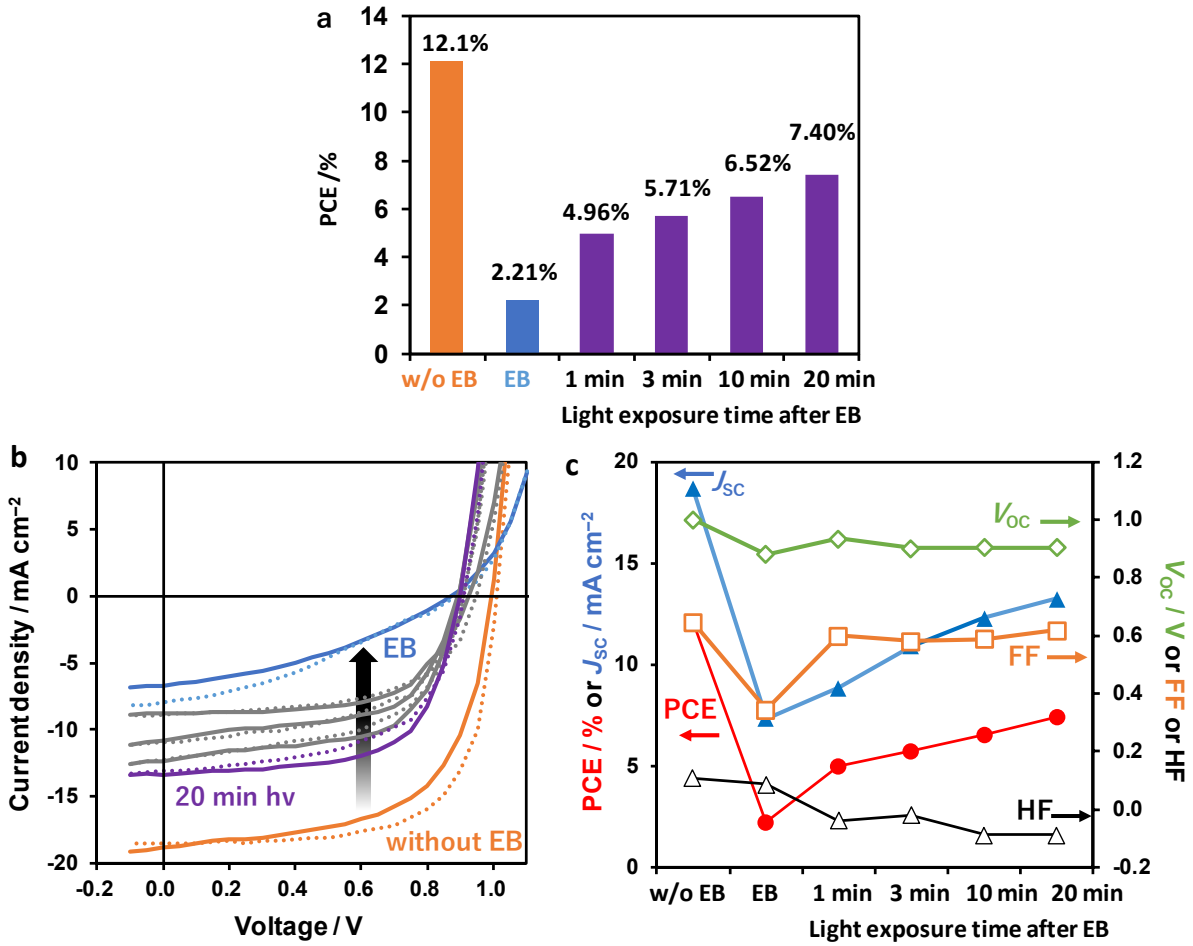

Figure S11. (a) PCE change of EB exposure and light treated PSC device. Note that this is the case for the low PCE device. (b) *JV* curves of PSC devices without EB (orange line), after 100 keV 2.5×10^{15} cm^{-2} EB exposure (blue line), AM1.5G 100 mW cm^{-2} light exposure (gray lines), and after 20 min light exposure (purple line). The solid and dotted lines are forward and reverse scans, respectively. (c) PCE, J_{SC}, V_{OC}, FF, and hysteresis factor (HF) without EB, EB, and light exposure.

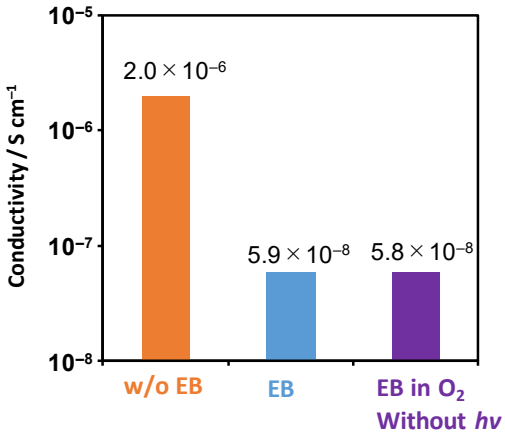

Figure S12. Steady-state conductivity of a SpiroOMeTAD without EB exposure (orange bar), after EB (100 keV, 2.5×10^{15} cm^{-2}) exposure (blue bar), and after the EB exposure and keeping in O_2 for 12 h without light exposure (purple bar).

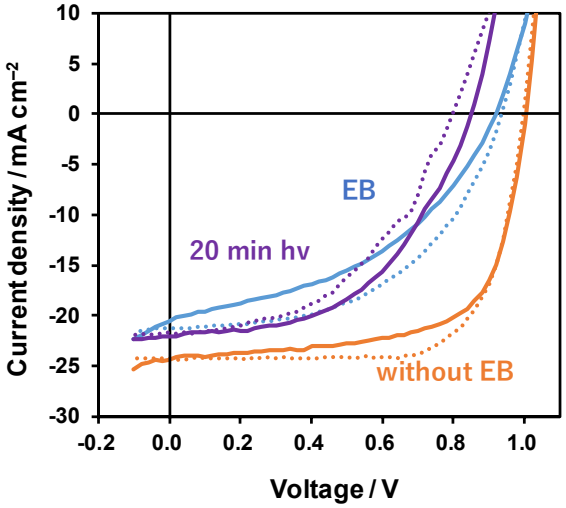

Figure S13. *JV* curves of PSC devices without EB (orange line), after 100 keV 2.5×10^{15} cm^{-2} EB exposure (blue line), and AM1.5G 100 mW cm^{-2} light exposure (purple line) under the short circuit condition for 20 min. The solid and dotted lines are forward and reverse scans, respectively.

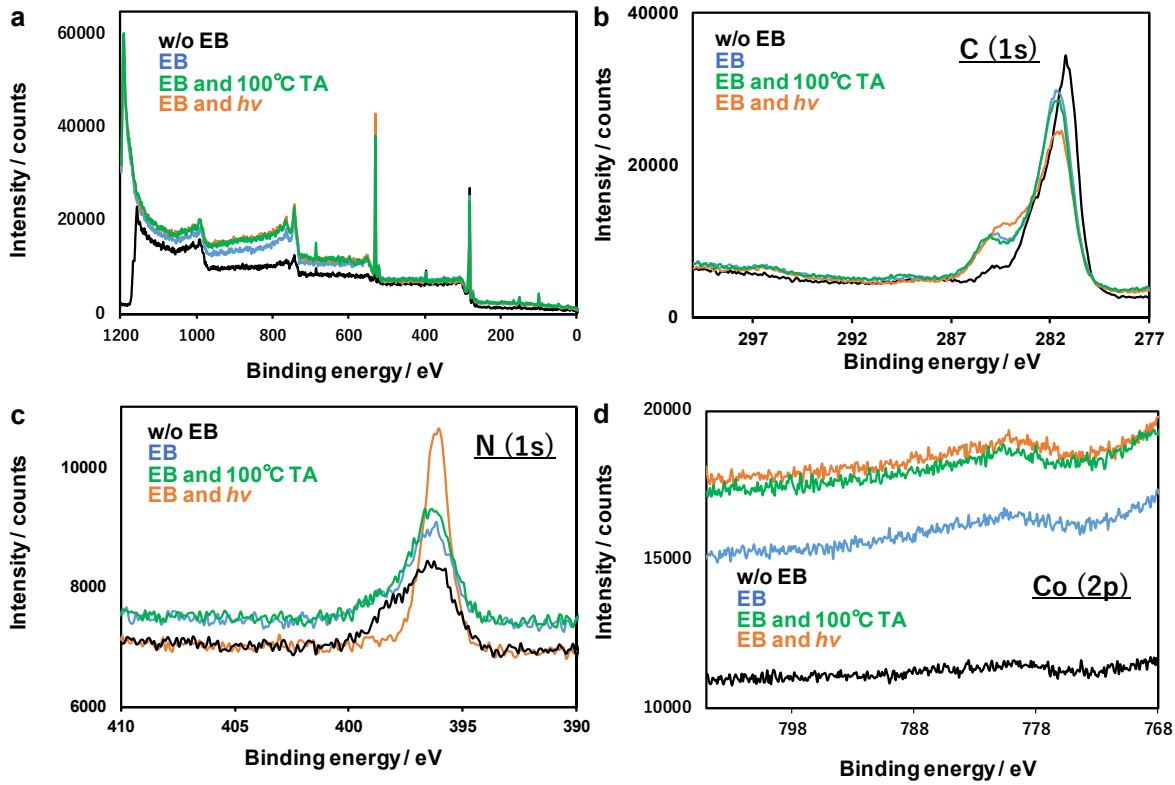

Figure S14. XP spectra of doped SpiroOMeTAD without EB (black line), EB (blue line, 100 keV, 2.5 × 10^{15} cm^{-2}), EB with 100 °C thermal annealing (green line), and EB with the lihgt treatment (*hv*: the psuedo sungliht at 100 mW cm^{-2} for 20 min) (orange line). (a) Full spectra and magnified plots at (b) C (1s) peak, (c) N (1s) peak, and (d) Cp (2p).

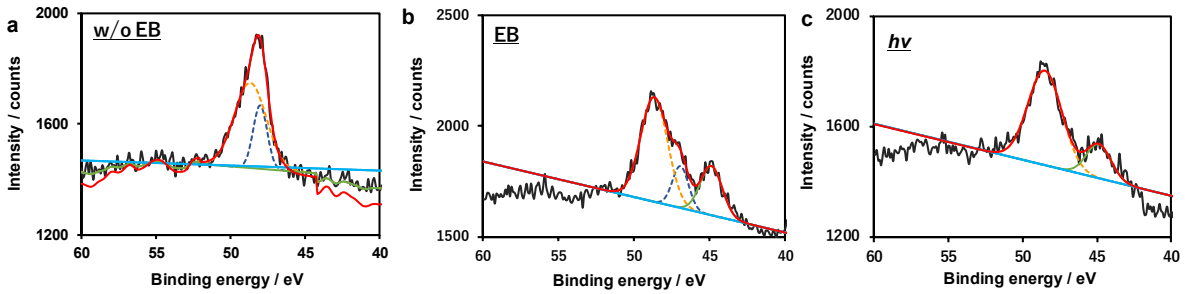

Figure S15. Fitting of XP spectra of doped SpiroOMeTAD (a) without EB, (b) EB (100 keV, 2.5×10^{15} cm^{-2}), and (c) EB with the lihgt treatment (*hv*: the psuedo sungliht at 100 mW cm^{-2} for 20 min).

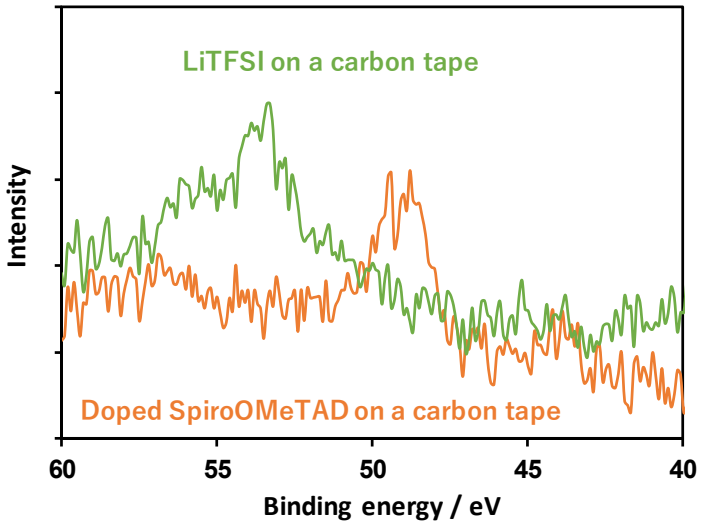

Figure S16. XP spectra of doped SpiroOMeTAD and LiTFSI powder on a carbon tape.

Table S1. Summary of perovskite solar cell before and after keeping in vacuum (0.5 Pa) for 30 min.[a]

Vacuum	PCE /%	J_{SC} /mA cm^{-2}	V_{OC} /V	FF	HF[b]	# of devices
Before	16.23±1.06 (17.68)	23.53±1.26 (24.17)	1.021±0.017 (1.037)	0.675±0.015 (0.694)	0.04±0.1 (0.02)	5
After	15.98±0.79 (17.24)	24.06±0.56 (25.01)	1.016±0.007 (1.006)	0.654±0.031 (0.676)	0.08±0.09 (0.01)	5

[a] The values in brackets are the maximum value. [b] hysteresis factor: [reverse – forward]/reverse.

Table S2. Summary of perovskite solar cell performance upon EB exposure (100 keV, 2.5 × 10^{15} cm^{-2}) and the light (AM1.5G, 100 mW cm^{-2}) treatment in O_2.

	PCE /%	J_{SC} /mA cm^{-2}	V_{OC} / V	FF	HF[a]	# of devices
w/o EB	16.64±0.20	25.55±0.15	0.963±0.007	0.676±0.011	0.06±0.03	3
EB	8.76±0.14	20.73±1.03	0.878±0.052	0.483±0.039	0.13±0.05	3
1 min	9.57±0.37	21.14±0.24	0.908±0.017	0.498±0.022	–0.03±0.15	3
3 min	10.51±0.12	21.14±0.17	0.896±0.003	0.554±0.006	–0.11±0.02	3
10 min	11.23±0.29	20.18±0.61	0.968±0.005	0.575±0.012	0.24±0.11	3
20 min	11.84±0.16	21.04±1.36	0.976±0.030	0.578±0.032	0.10±0.08	3

[a] hysteresis factor: [reverse – forward]/reverse.

Table S3. Summary of perovskite solar cell performance upon EB exposure (100 keV, 2.5 × 10^{15} cm^{-2}) and the light (AM1.5G, 100 mW cm^{-2}) treatment under the short circuit condition in O_2

	PCE /%	J_{SC} /mA cm^{-2}	V_{OC} / V	FF	HF[a]	# of devices
w/o EB	16.66±0.16	24.43±0.38	0.982±0.016	0.694±0.004	0.05±0.03	3
EB	8.90±0.35	21.03±0.41	0.892±0.070	0.475±0.012	0.19±0.08	3
20 min	8.83±0.03	21.61±0.42	0.846±0.040	0.483±0.013	–0.10±0.09	3

[a] hysteresis factor: [reverse – forward]/reverse.