Electronic Supplementary Information (ESI)

Exploration of Charge Transport Materials to Improve the Radiation Tolerance of Lead Halide Perovskite Solar Cells

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Supplementary Tables S1–S2

Supplementary Figure S1–S16

Supplementary Reference S1

Table S1. Normalized $\varphi\Sigma\mu_{max}$ and τ (lifetime) of EB (2.5×10^{15} cm^{-2})-exposed films relative to those without EB expsoure.

HTM or ETM	Normalized $\varphi\Sigma\mu_{max}$	τ[a]
C_{60}	0.70±0.07	1.08±0.11
PCBM	0.65±0.10	0.97±0.41
CuSCN	0.55±0.10	0.59±0.07
PTB7	0.85±0.12	0.99±0.06
PTAA	0.70±0.08	0.98±0.15

[a] The τ was obtained by fiting the double exponential functions ($A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$) to the kinetics and calculating the effective lifetimes ($\tau = (A_1\tau_1 + A_2\tau_2)(A_1 + A_2)^{-1}$). The values are normalized by τ before EB exposure.

Table S2. EB effect on hole transport yield (TiO_2/Perovskite/PTB7 or PTAA).[a]

HTM	EB exposure	η_0	η_{sat}	k (s^{-1})
PTB7	Before EB	0.33	0.96	1.26×10^6
	After EB ($F_{EB} = 2.5\times10^{15}$ cm^{-2})	0.22	0.58	8.64×10^4
PTAA	Before EB	0.21	0.95	1.51×10^6
	After EB ($F_{EB} = 2.5\times10^{15}$ cm^{-2})	0.28	0.93	7.55×10^5

[a] η_0, η_{sat}, and k were obtained from the analysis of decay fitting. The details are reported in the literature.[S1]

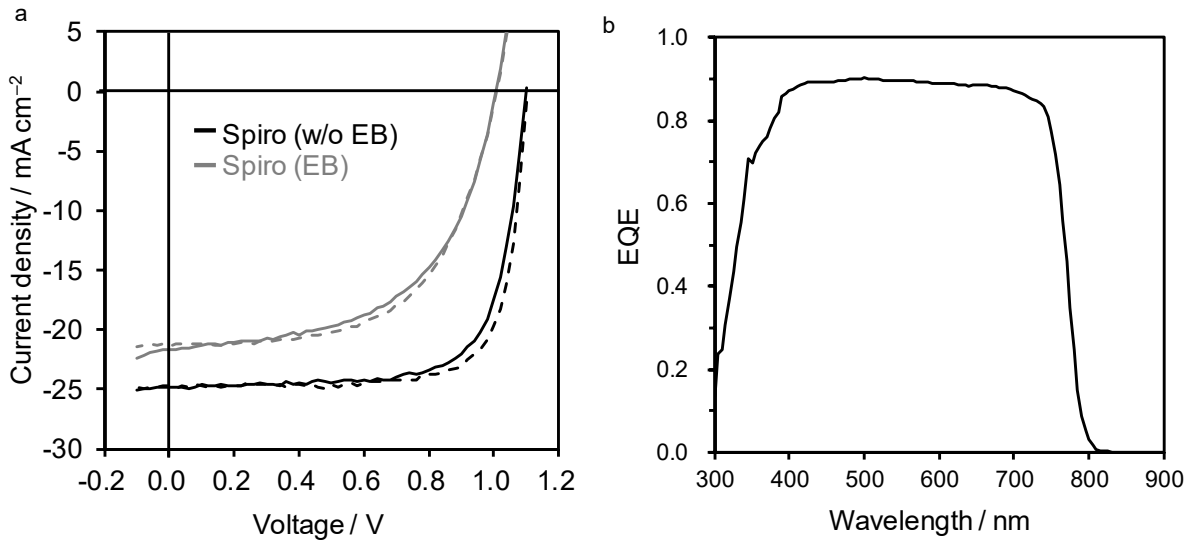

Figure S1. (a) *JV* curves of Device 1 (FTO/c-TiO_2/mpTiO_2/PVK/Spiro-OMeTAD/Au) without EB exposure (black lines) and after 2.5×10^{15} cm^{-2} exposure (gray lines). The solid and dotted lines are the forward and reverse scans, respectively. (b) EQE spectrum of Device 1 without EB. The maximum value is 0.90 at ~500 nm, and the onset is ~815 nm. The J_{SC} calculated by integrating the EQE spectrum is 22.1 mA cm^{-2}, which is smaller than the J_{SC} under 1 sun (25.3 mA cm^{-2}; 13% difference). Note that the light intensities of our EQE instrument and solar simulator were calibrated by a standard cell, and a good match (<±2% difference) is obtained for organic solar cells. The small J_{SC} in EQE of PSC may be due to the trap filling under a stronger white light intensity of a solar simulator (our EQE facility does not provide a white light bias, and thus, the EQE is measured upon the exposure to a weaker intensity of light).

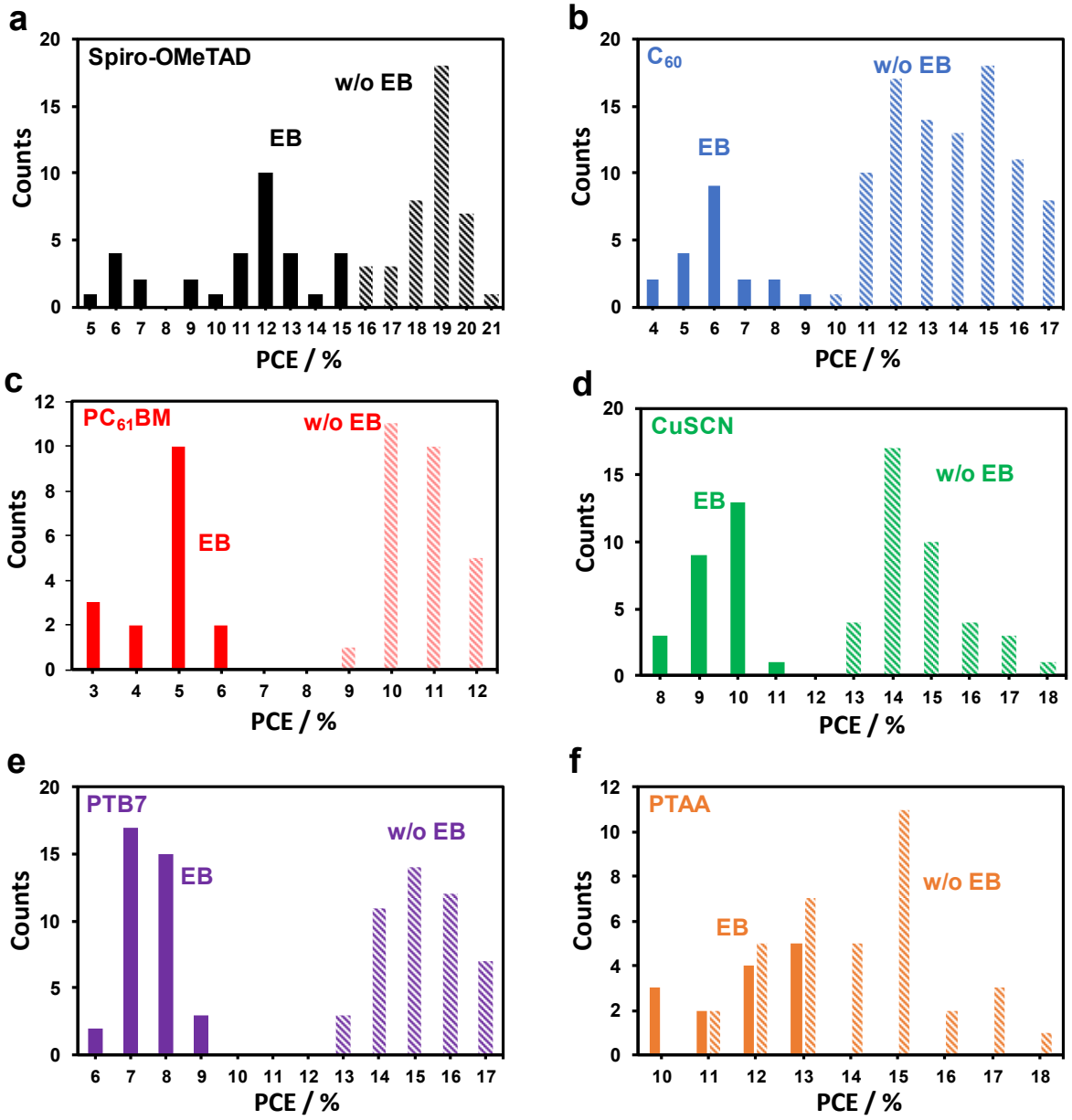

Figure S2. Histograms of the PCE values of each PSC without EB exposure (solid bar) and after 2.5×10^{15} cm^{-2} exposure (meshed bar). (a) Spiro-OMeTAD (b) C_{60} (c) PCBM (d) CuSCN (e) PTB7 (f) PTAA.

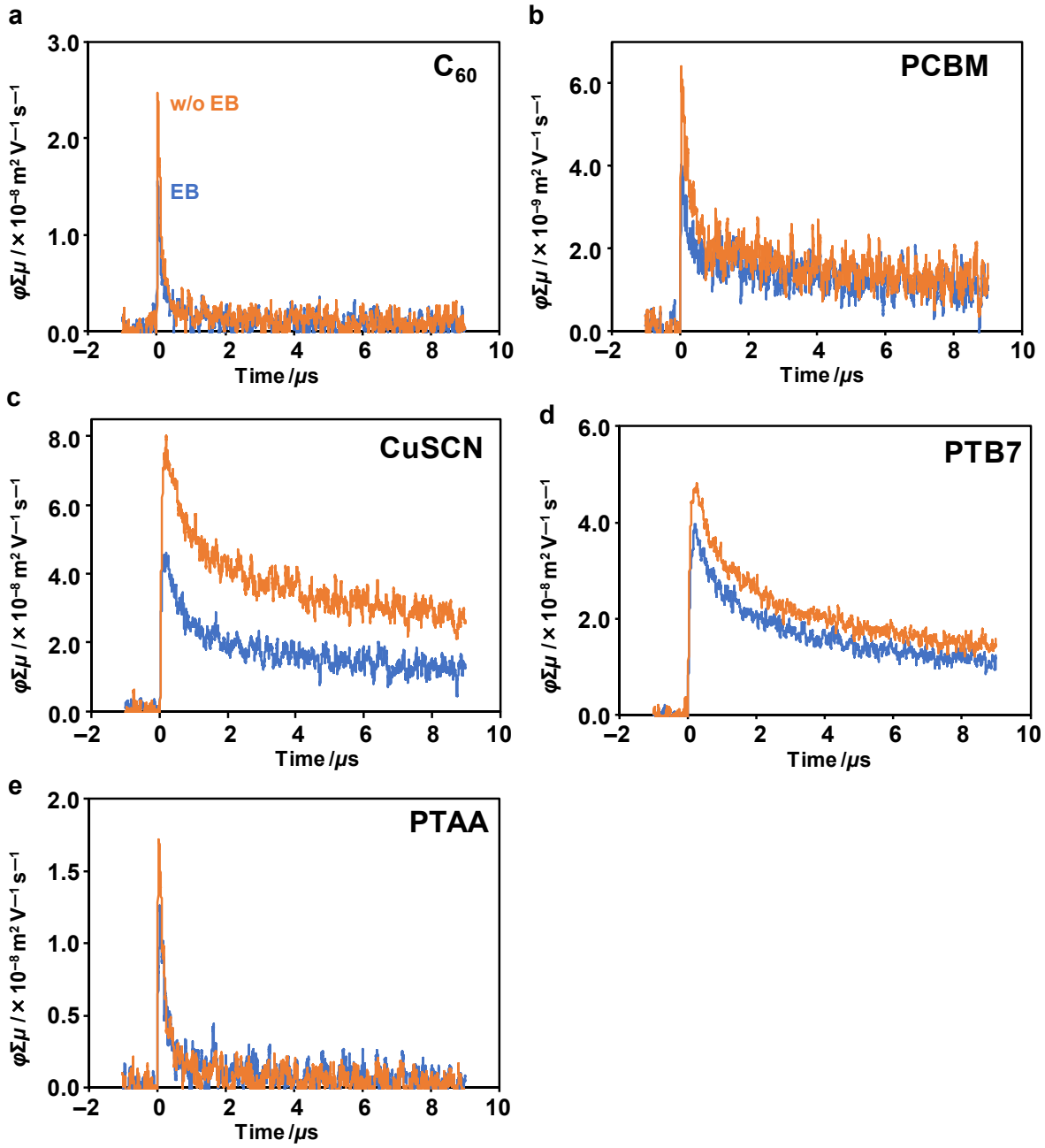

Figure S3. TRMC transients (λ_{ex} = 355 nm) of (a) C_{60} (b) $PC_{61}BM$ (c) CuSCN (d) PTB7 (e) PTAA with EB exposure of 2.5 × 10^{15} cm^{-2} (blue line) and without EB exposure (blue line). Photon density I_0 = 7.0 × 10^{15} photons cm^{-2} $pulse^{-1}$ (C_{60}), 1.3 × 10^{16} photons cm^{-2} $pulse^{-1}$ (PTAA), or 2.0 × 10^{16} photons cm^{-2} $pulse^{-1}$ (PCBM, CuSCN, and PTB7).

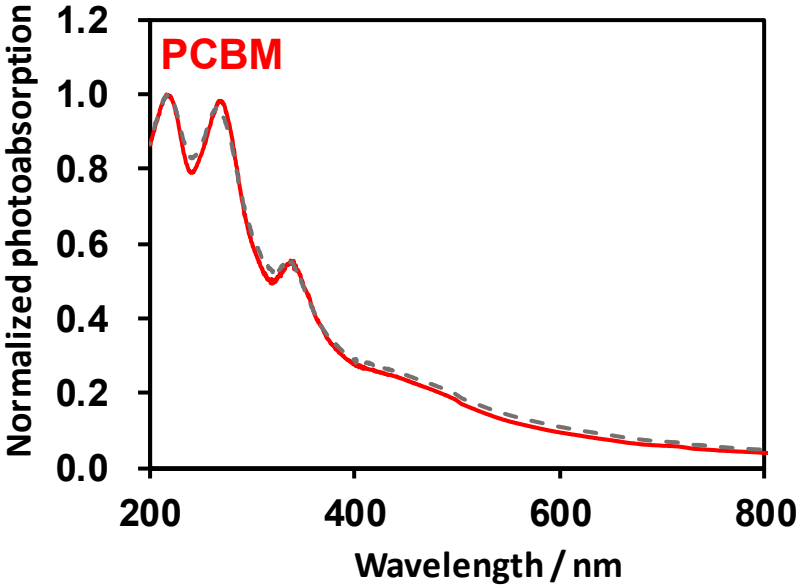

Figure S4. UV-visible photoabsorption spectra of PCBM film without EB (dotted line) and after EB exposure (solid red line).

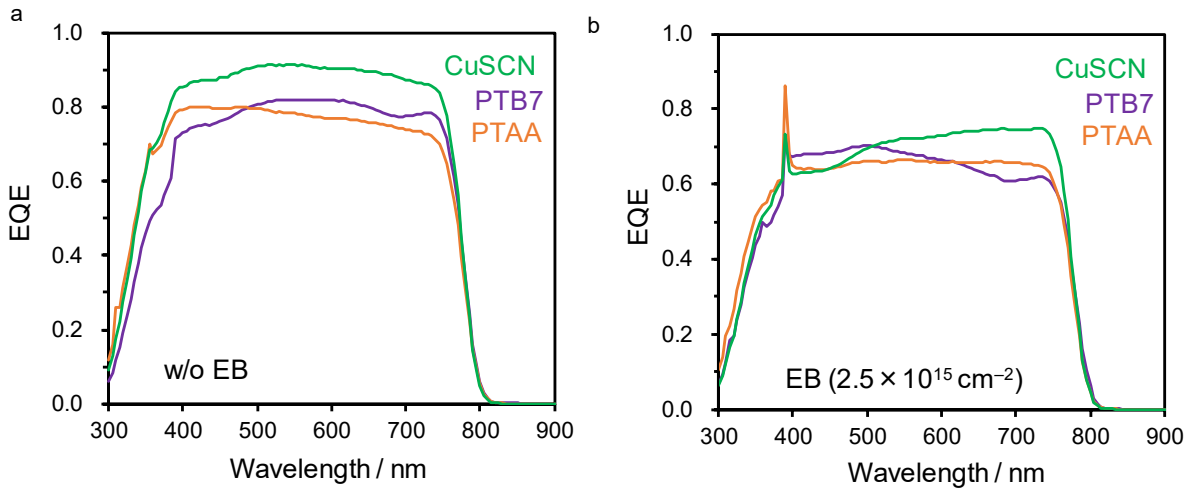

Figure S5. (a) EQE spectra of Device 4 (CuSCN), Device 5 (PTB7), and Device 6 (PTAA) without EB. Their maximum values are 0.92, 0.82, and 0.80, respectively. The onset is ~815 nm. The J_{SC} calculated by integrating the EQE spectrum is 22.4, 20.0, and 19.5 mA cm^{-2}, respectively. They are smaller than the J_{SC} under 1 sun (24.9, 24.2, and 25.7 mA cm^{-2}, respectively). Note that the light intensities of our EQE instrument and solar simulator were calibrated by a standard cell, and a good match (<±2% difference) is obtained for organic solar cells. The small J_{SC} in EQE of PSC may be due to the trap filling under a stronger white light intensity of a solar simulator (our EQE facility does not provide a white light bias, and thus, the EQE is measured upon the exposure to a weaker intensity of light). (b) EQE spectra of Device 4 (CuSCN), Device 5 (PTB7), and Device 6 (PTAA) after EB exposure (2.5×10^{15} cm^{-2}). The calculated J_{SC}s are 18.1, 16.7, and 16.6 mA cm^{-2}, respectively.

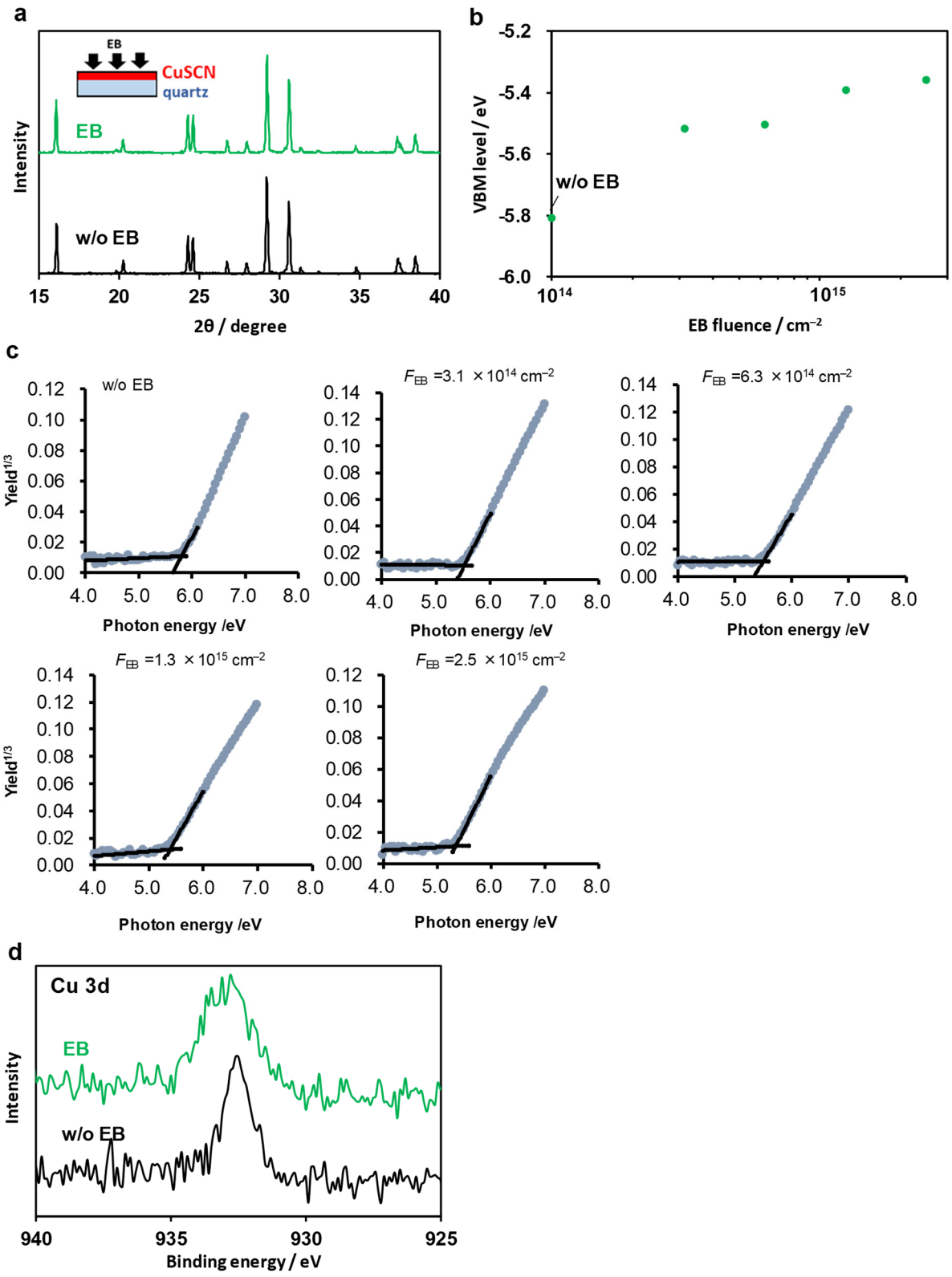

Figure S6. (a) XRD profiles of CuSCN without (black) and with EB (F_{EB} = 2.5 × 10^{15} cm^{-2}) exposure. (b) VBM level of CuSCN after EB exposure. The point at F_{EB} = 10^{14} cm^{-2} is the value without EB exposure. (c) PY spectra of CuSCN. The black lines are fitting to calculate the onset photon energy. (d) XPS profiles of Cu-3d states of CuSCN.

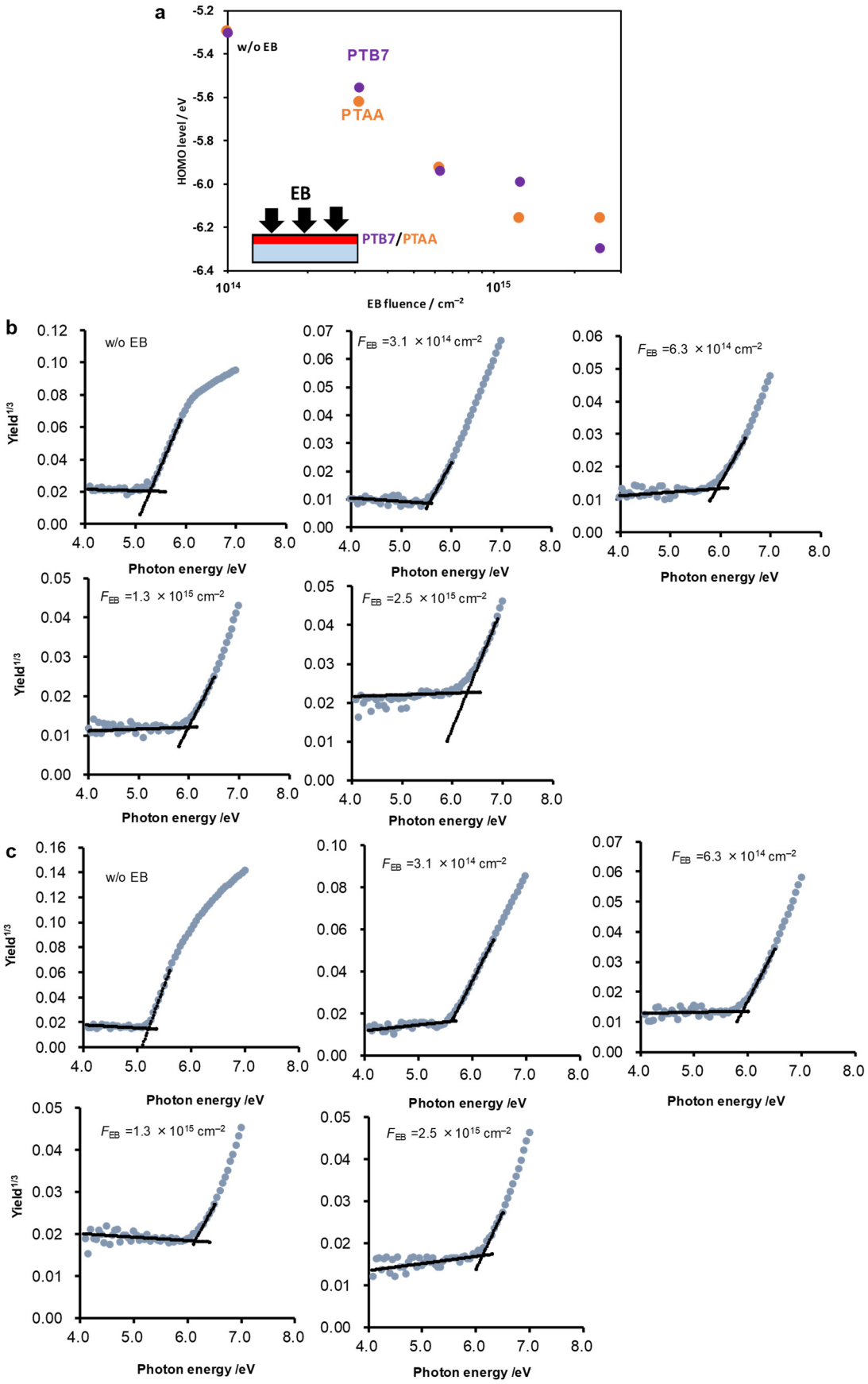

Figure S7. (a) HOMO level of PTB7 and PTAA without EB exposure and after EB exposure, which was measured by PYS. (b) PY spectra of PTB7 with/without EB. (c) PY spectra of PTAA with/without EB.

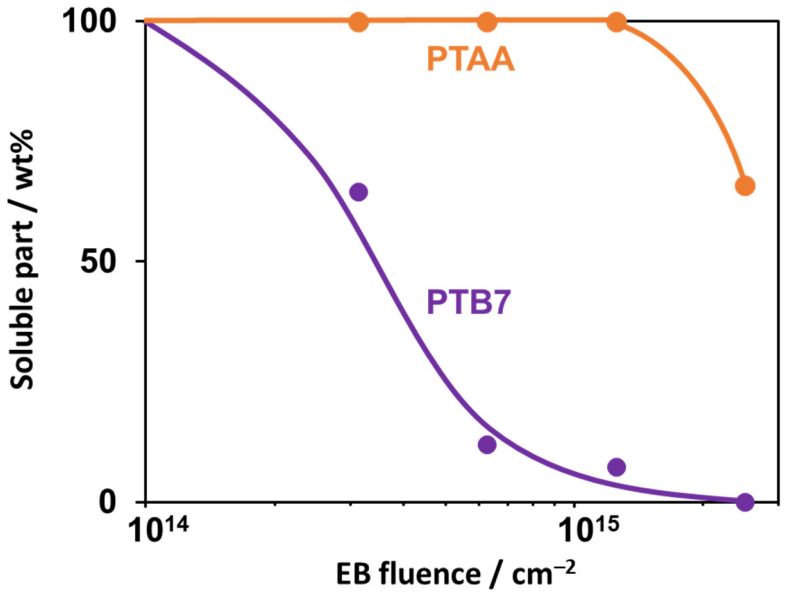

Figure S8. Weight fraction of soluble part of PTB7 and PTAA in chloroform after EB exposure.

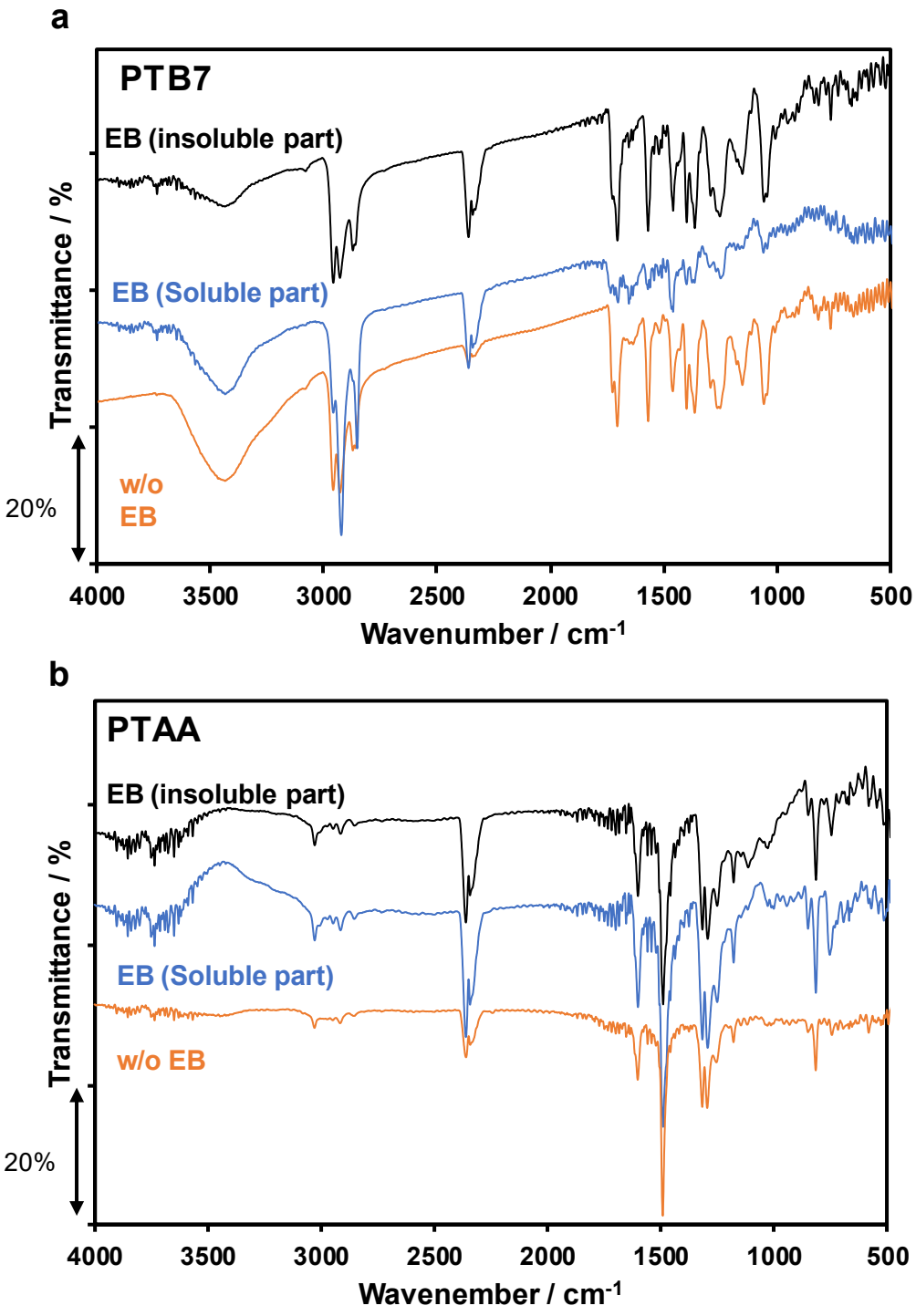

Figure S9. FT-IR spectra (KBr) of (a) PTB7 (F_{EB} = 3.1 × 10^{14} cm^{-2}) and (b) PTAA (F_{EB} = 2.5 × 10^{15} cm^{-2}).

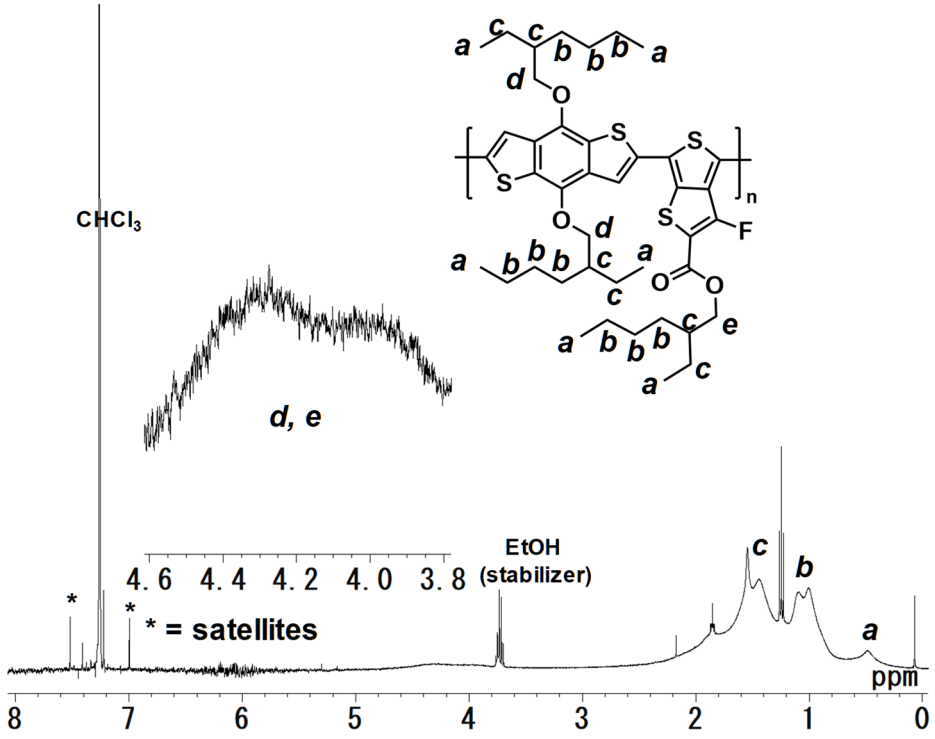

Figure S10. NMR chart of PTB7 without EB exposure (400 MHz, $CDCl_3$, 25 °C).

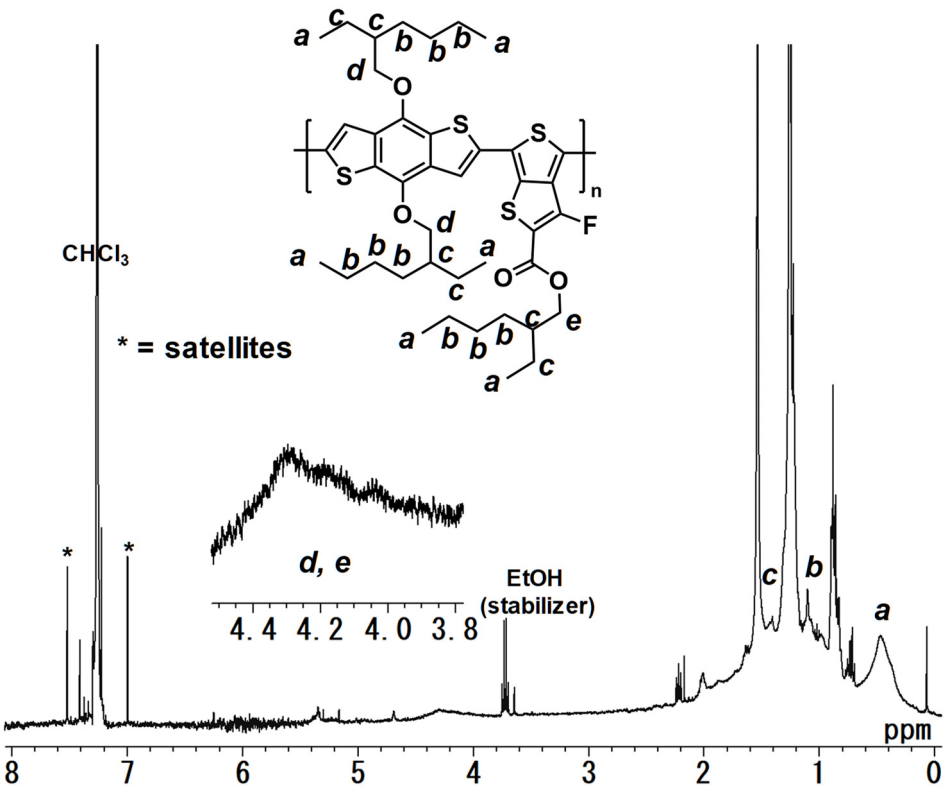

Figure S11. NMR chart of PTB7 and after 2.5×10^{15} cm^{-2} EB exposure (400 MHz, $CDCl_3$, 25 °C).

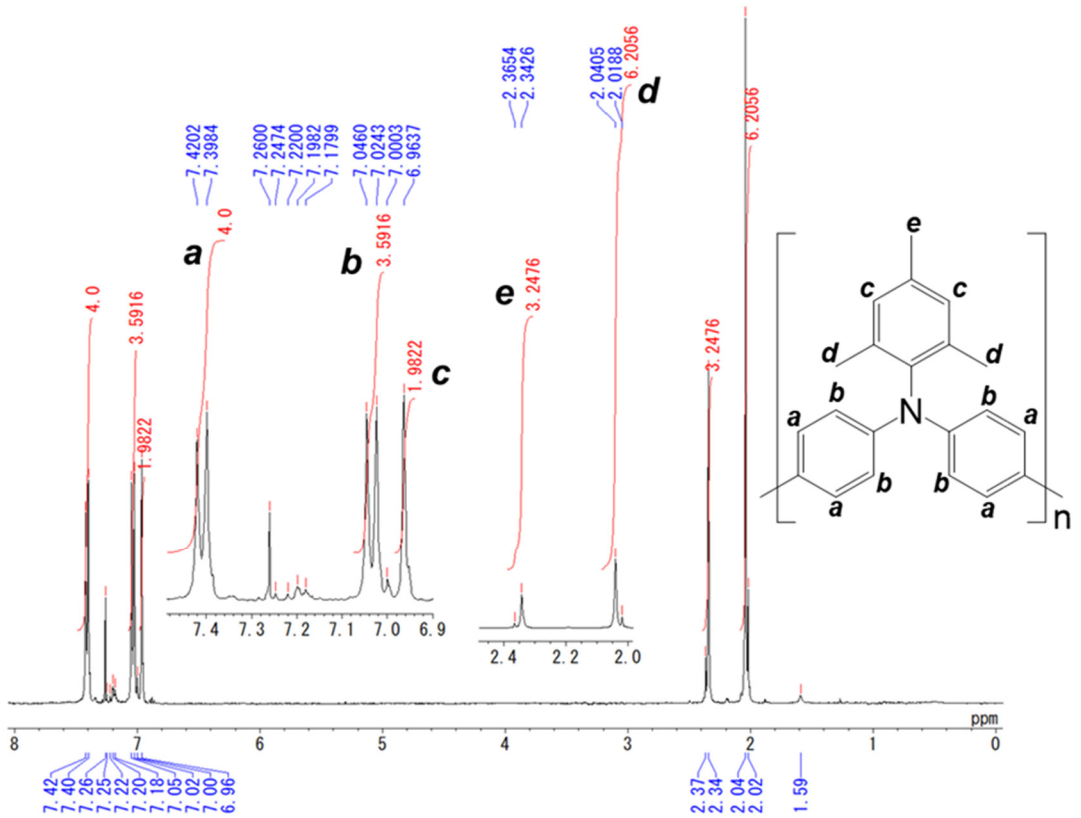

Figure S12. NMR chart of PTAA without EB exposure (400 MHz, $CDCl_3$, 25 °C).

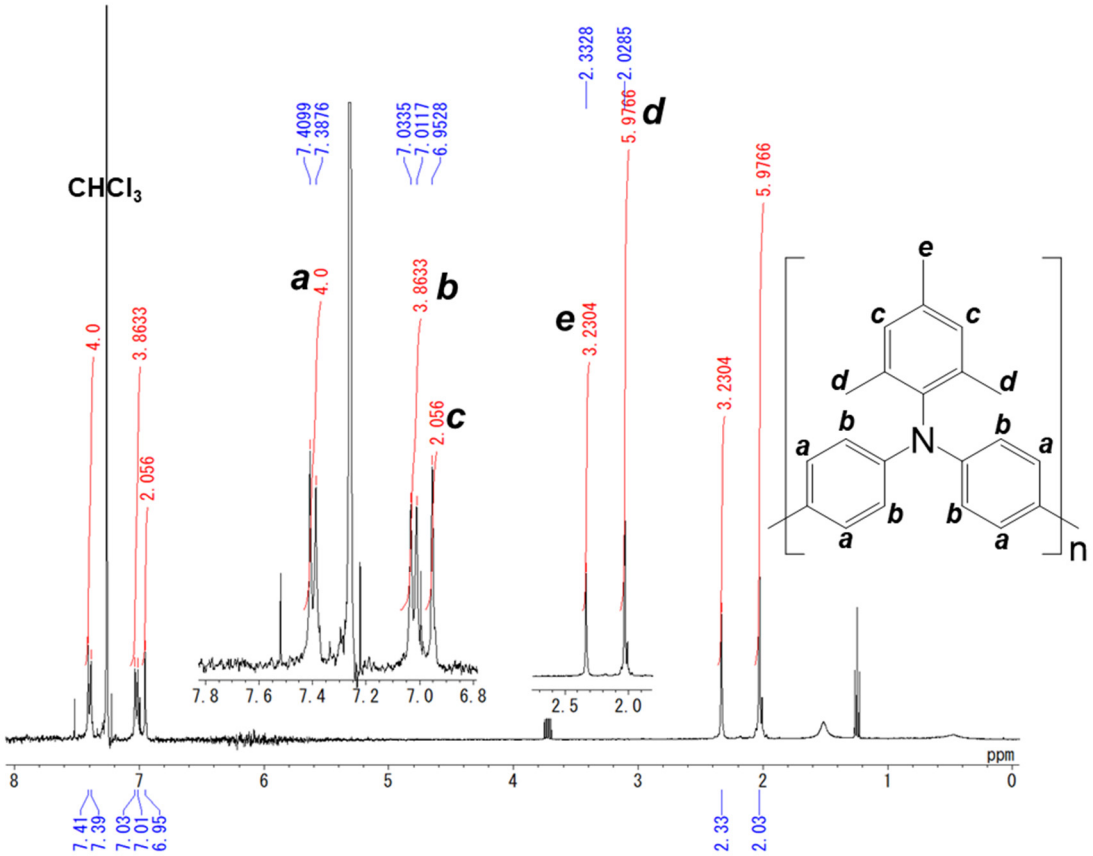

Figure S13. NMR chart of PTAA after 2.5 × 10^{15} cm^{-2} EB exposure (400 MHz, $CDCl_3$, 25 °C).

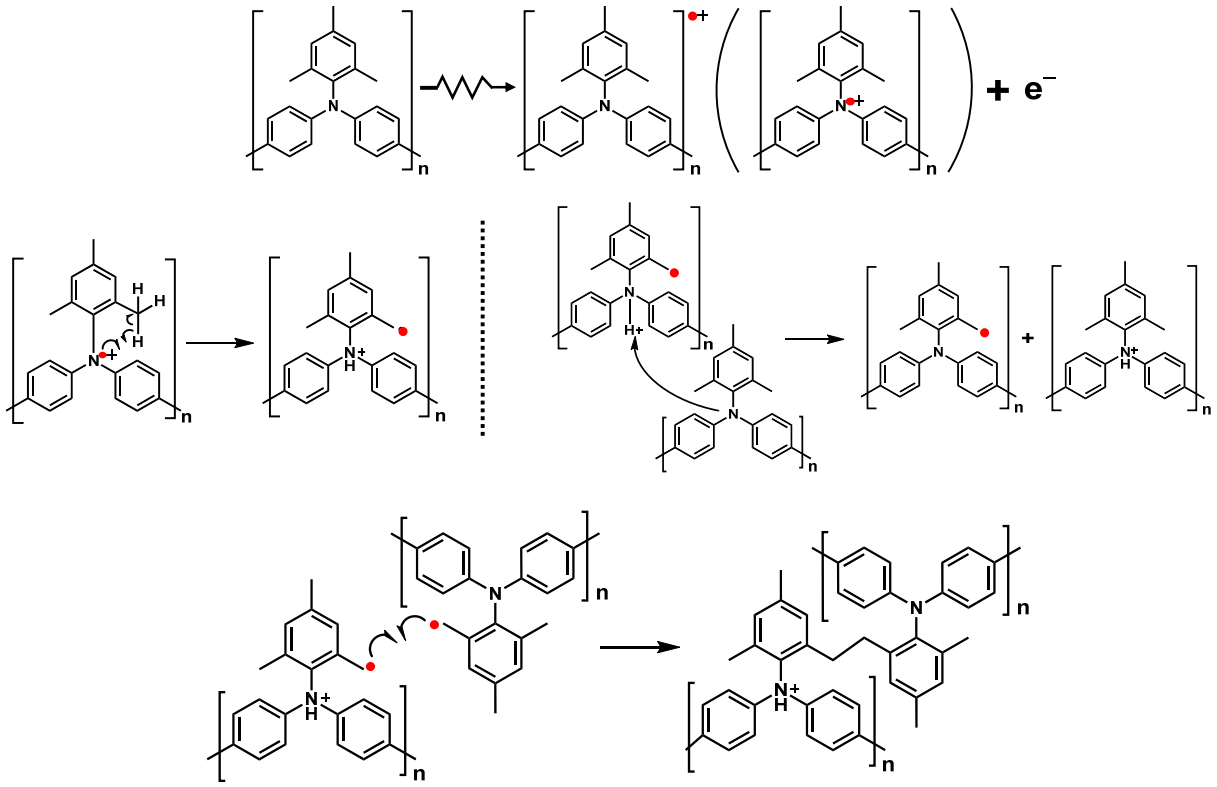

Figure S14. Possible mechanism of PTAA crosslinking upon EB expsoure. The radical is illustrated by the red circles.

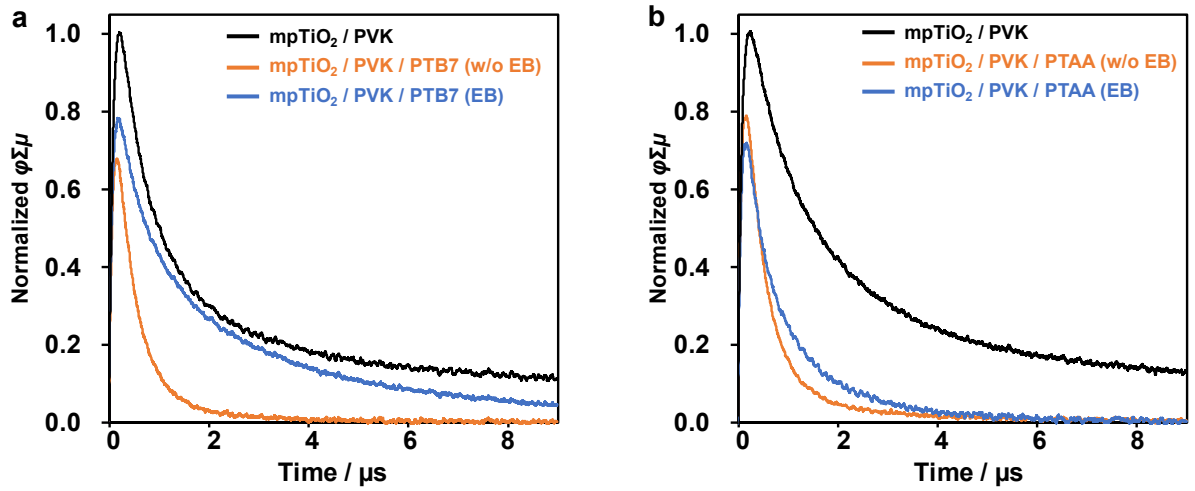

Figure S15. Noramlized TRMC transients (λ_{ex} = 500 nm) of (a) mp-TiO_2 / PVK / PTB7 (b) mp-TiO_2 / PVK / PTAA (F_{EB} = 2.5 × 10^{15} cm^{-2}).

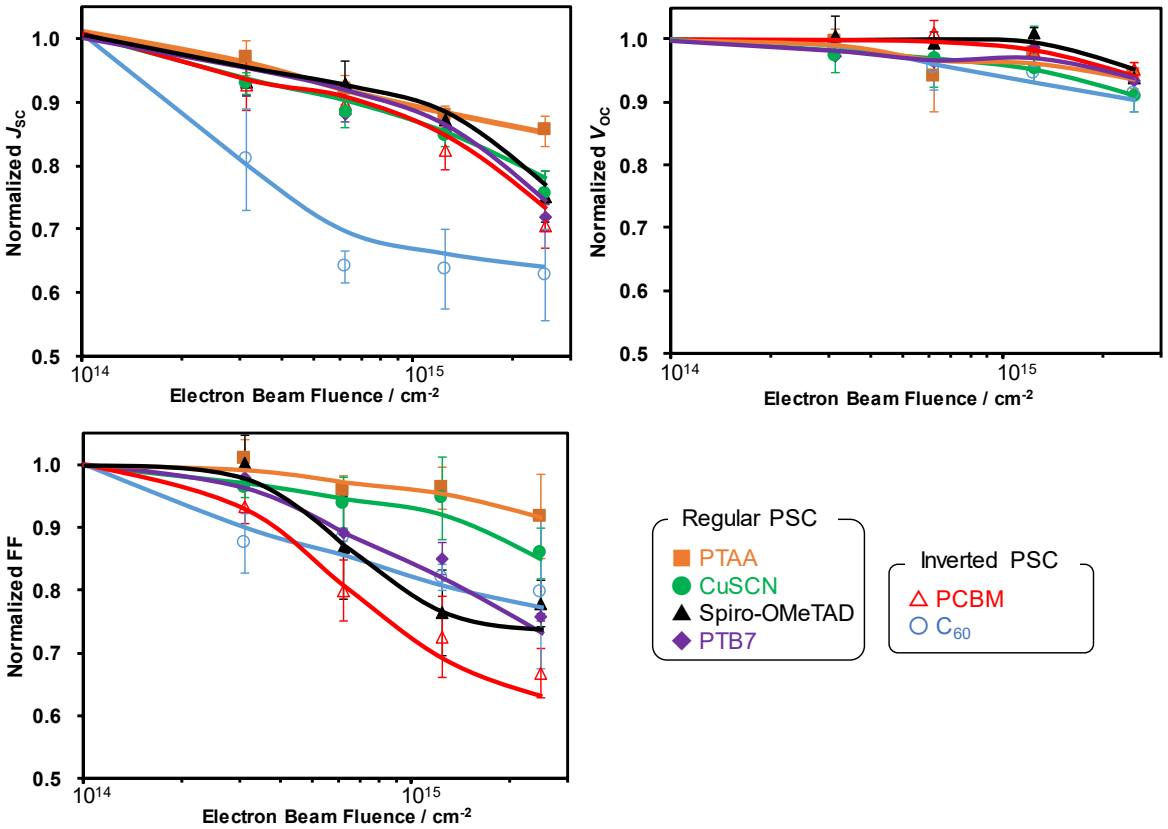

Figure S16. Normalized values of J_{SC}, V_{OC}, and fill factor.

Supplementary references

(S1) N. Ishida, A. Wakamiya and A. Saeki, *ACS Photonics* 2016, **3**, 1678.