

## Supplementary Document

### High-efficiency (>30%) monolithic perovskite-Si tandem solar cells with flat front-side wafers

5

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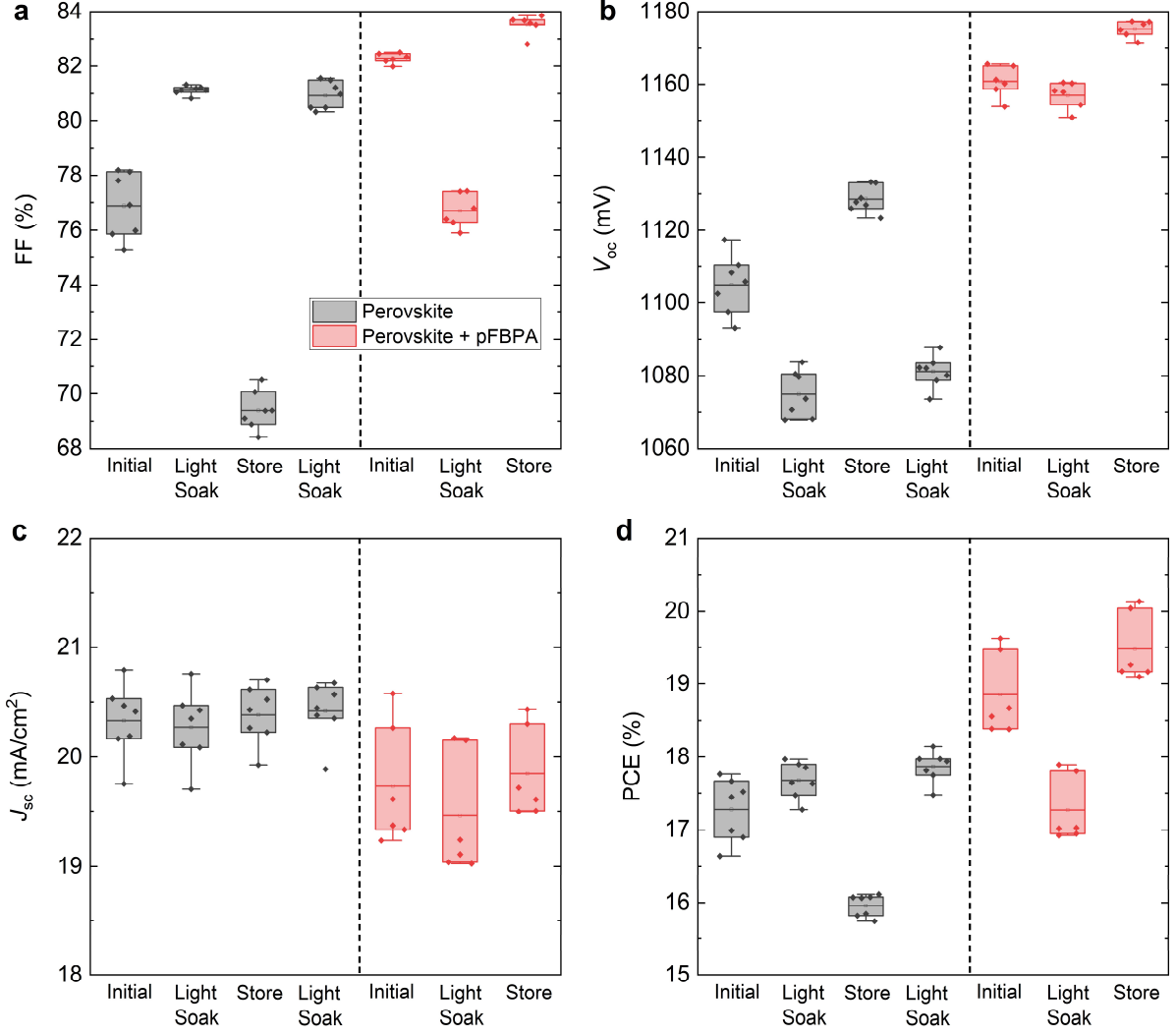
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10

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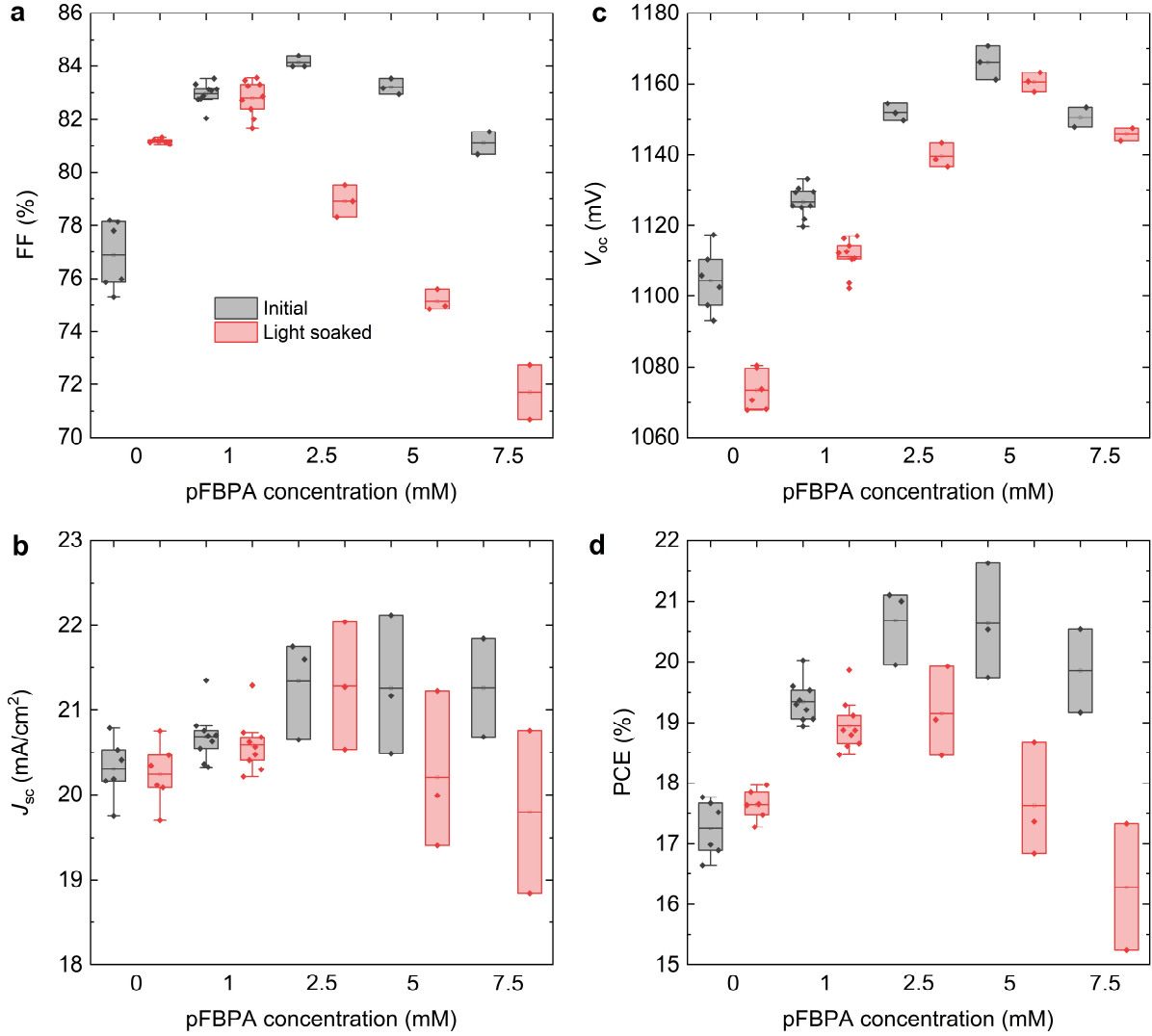
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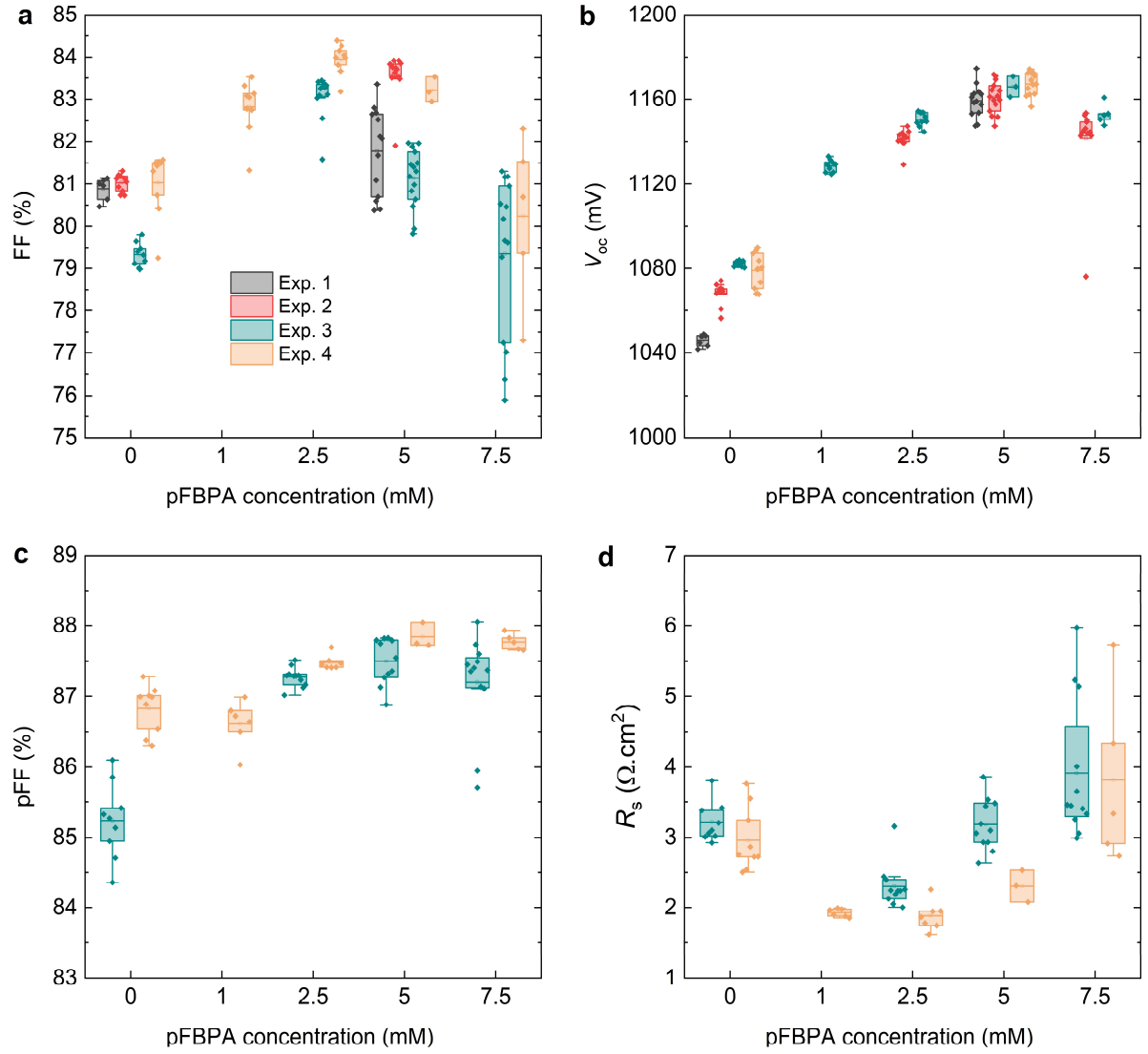


**Fig. S1. Light-soaking under open-circuit and storage under dark in N<sub>2</sub>-filled glovebox. a-d,** Fill factor (FF) (a), short-circuit current density ( $J_{sc}$ ) (b), open-circuit voltage ( $V_{oc}$ ) (c) and power conversion efficiency (PCE) (d) of 0.1 cm<sup>2</sup> single-junction perovskite solar cells without and with 5 mM pFBPA included in the perovskite precursor. The cells have an ITO/Me-4PACz/SiO<sub>2</sub>-NP stack as the hole-transport layer. The cells are measured in various stages - including an initial measurement after the completion of device fabrication (i.e., 'Initial'), after light soaking under 1-sun illumination for 3 min at open circuit (i.e., 'Light soak'), storing in N<sub>2</sub>-filled glovebox for ~12 hr (i.e. 'Store').

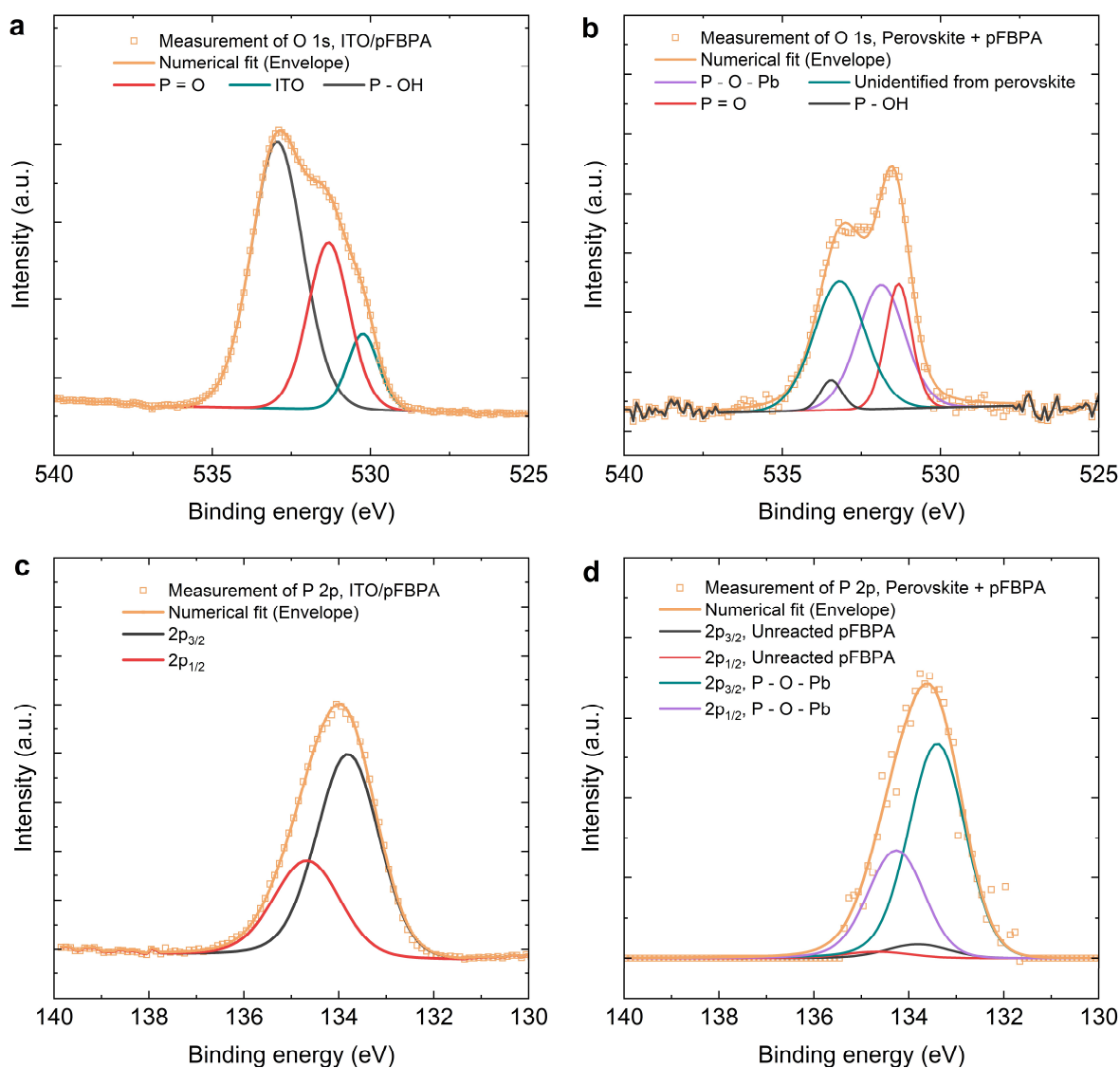




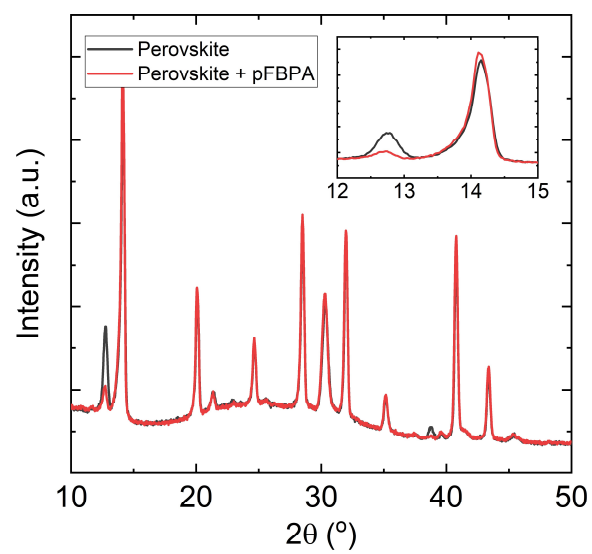
**Fig. S2. Effect of pFBPA concentration on light soaking response at open-circuit.** a-d, Fill factor (FF) (a), short-circuit current density ( $J_{sc}$ ) (b), open-circuit voltage ( $V_{oc}$ ) (c) and power conversion efficiency (PCE) (d) of 0.1 cm<sup>2</sup> single-junction perovskite solar cells with various concentrations of pFBPA included in the perovskite precursor. The cells have an Me-4PACz/SiO<sub>2</sub>-NP stack as the hole-transport layer. They are measured in two stages - an initial measurement after the completion of device fabrication (i.e., 'Initial'), after light soaking under 1-sun illumination for 3 min at open circuit (i.e., 'Light soak').



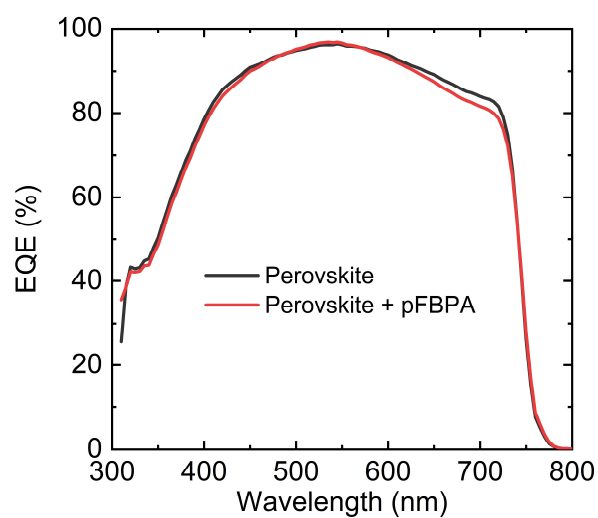
**Fig. S3. Perovskite cells with Me-4PACz/SiO<sub>2</sub>-NP with varying pFBPA concentration.** a-d, Open-circuit voltage ( $V_{oc}$ ) (a), fill factor (FF) (b), pseudo-FF (c), and series resistance near maximum power point ( $R_s$ ) (d) of 0.1 cm<sup>2</sup> single-junction perovskite solar cells on glass/ITO/Me-4PACz/SiO<sub>2</sub>-NP substrates, with various concentrations of pFBPA included in the perovskite precursor. The experiment is repeated four times, denoted with the different experiment numbers in the legend.



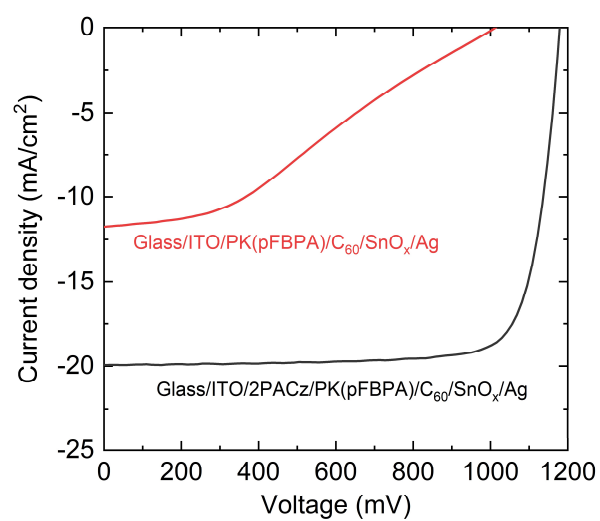
**Fig. S4. XPS spectra.** a-d, X-ray photoelectron spectroscopy (XPS) measurements (yellow line) and numerically fit constituents of the O 1s (a) and P 2p (c) core levels for ITO/pFBPA and O 1s (b) and P 2p (d) core levels perovskite samples with 5 mM of pFBPA in the precursor. The square hollow symbols indicate the measurement outputs and the lines indicate the numerical fitting outputs.



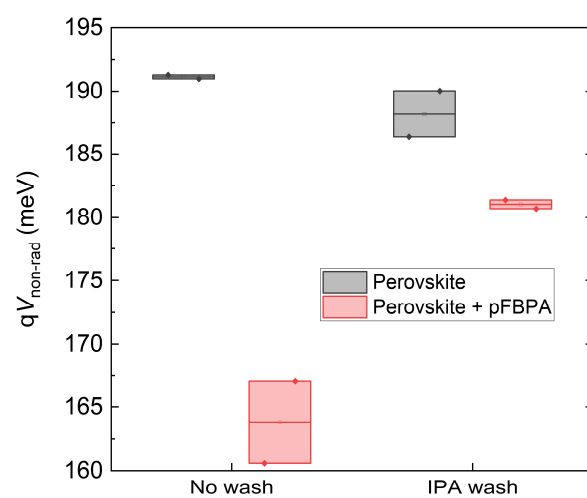
**Fig. S5. XRD of the films with and without pFBPA.** X-ray diffraction (XRD) measurement results of bare perovskite films without and with 5 mM of pFBPA in the precursor. The films are deposited on glass/ITO/2PACz substrates.



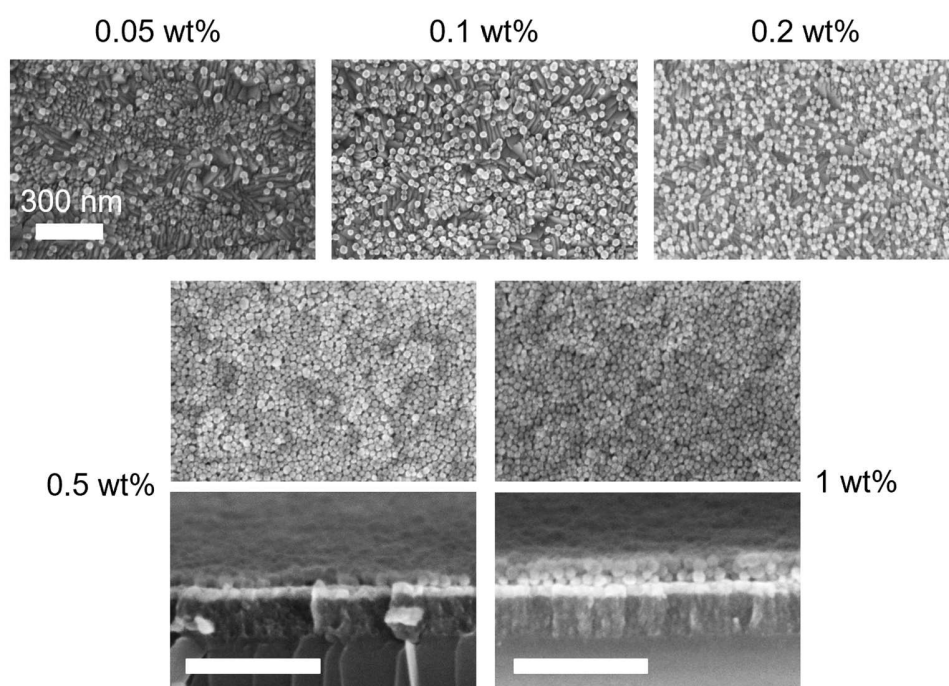
**Fig. S6. Effect of pFBPA on the spectral response of the perovskite cell in a tandem device** – External quantum efficiency (EQE) spectra of perovskite top cells in perovskite-Si tandem devices, without and with 5 mM of pFBPA in the perovskite precursor. The results indicate a constant bandgap, but a decreasing thickness (by ~50 nm) with pFBPA use.



**Fig. S7. Perovskite absorbers on glass/ITO substrates with and without an HTL** - Current density versus voltage for 0.1 cm<sup>2</sup> single-junction perovskite cells with 5 mM of pFBPA in the perovskite precursor (i.e., 'PK(pFBPA)'), with and without a 2PACz hole transport layer on the glass/ITO substrate.

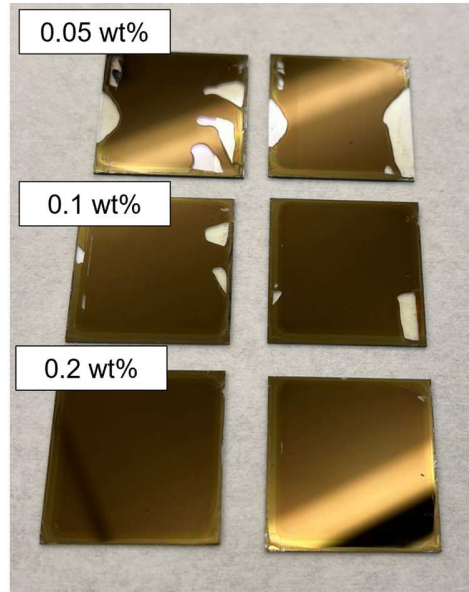


**Fig. S8. Effect of perovskite surface washing on passivation by pFBPA** - Non-radiative recombination losses ( $qV_{\text{non-rad}}$ ) of glass/ITO/2PACz/perovskite/ $C_{60}$  samples with and without 5 mM pFBPA in the precursor, and with and without a subsequent 2-propanol (IPA) washing. The washing is performed by dropping 100  $\mu\text{L}$  of IPA on a sample rotating at 3500 rpm.

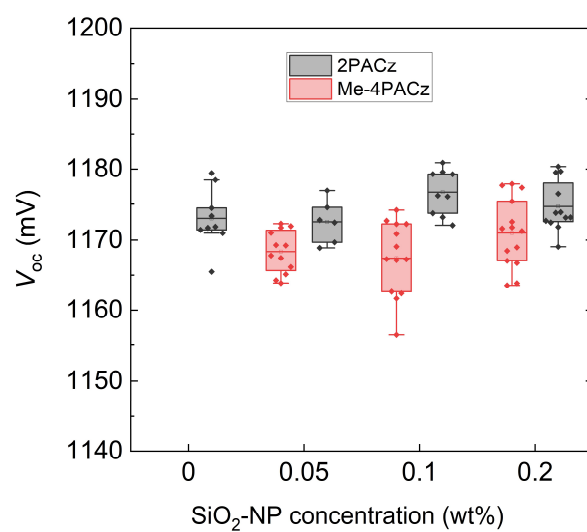


**Fig. S9. SiO<sub>2</sub>-NPs on ITO.** Scanning electron microscope images of SiO<sub>2</sub>-NP coated samples with varying concentrations of SiO<sub>2</sub>-NP in the dispersion (from 0.05 to 1 wt%) as specified in text next to the images. For all samples, the images are taken from a top view. For 0.5 and 1 wt%, the tilted cross section images are also included.

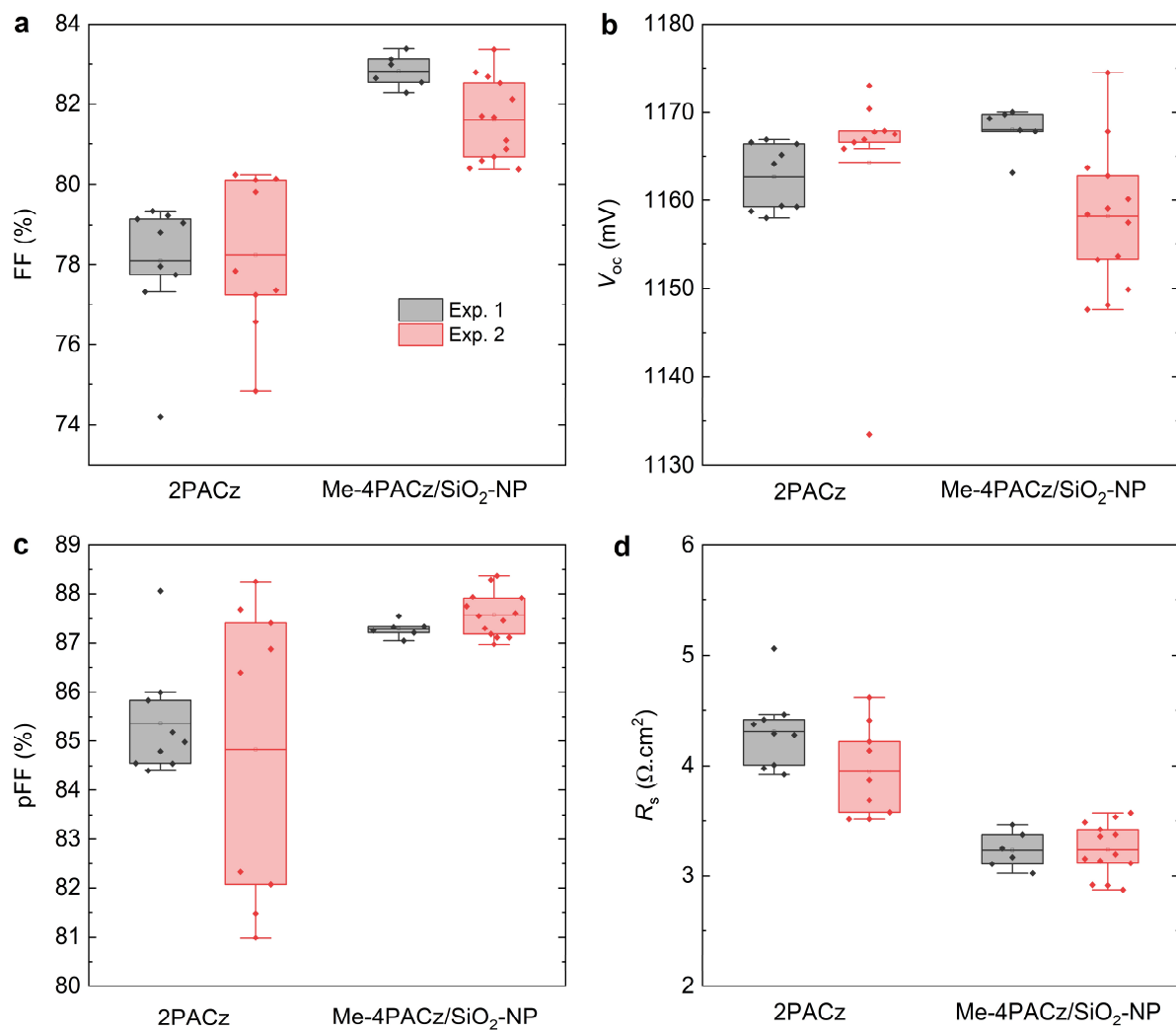




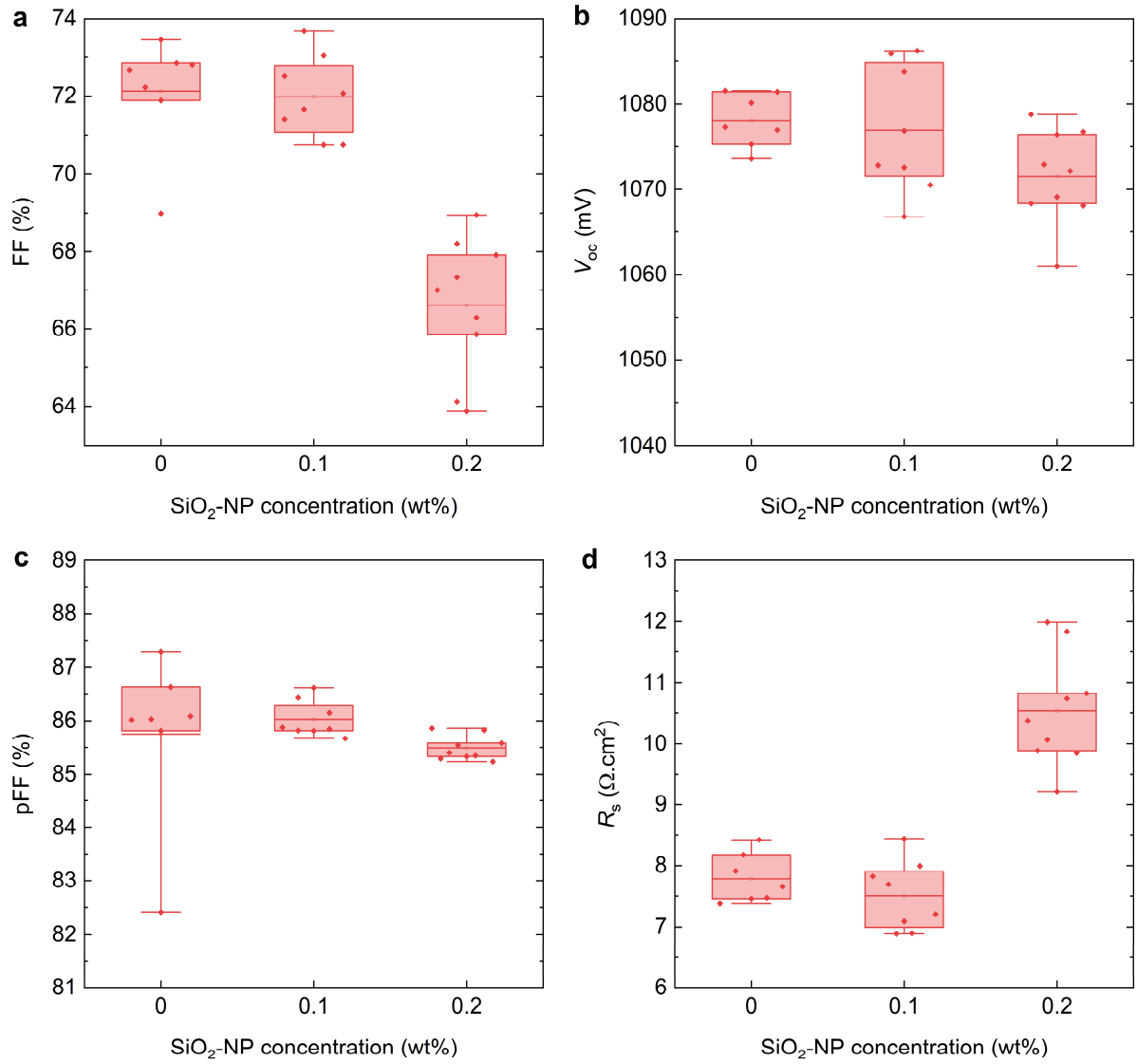
**Fig. S10. Enhanced surface wettability of Me-4PACz by SiO<sub>2</sub>-NPs.** Perovskite films coated on glass/ITO/Me-4PACz/SiO<sub>2</sub>-NP substrates with varying concentrations of SiO<sub>2</sub>-NP dispersions that are specified in the text boxes in the image. The ITO is etched on two opposite sides of the substrates (by 5 mm from the edges).



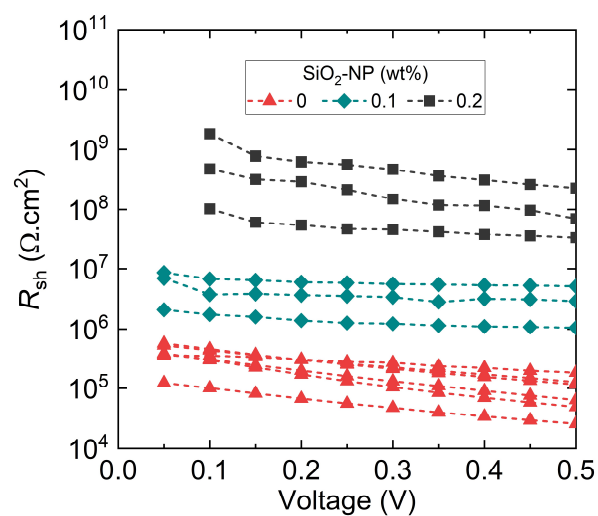
**Fig. S11. Response of  $V_{oc}$  with varying SiO<sub>2</sub>-NP concentration.** Open-circuit voltage ( $V_{oc}$ ) of perovskite cells fabricated on glass/ITO/Me-4PACz and 2PACz substrates with varying concentrations of SiO<sub>2</sub>-NP dispersions. The other cell parameters are shown in Fig. **2b-d**.



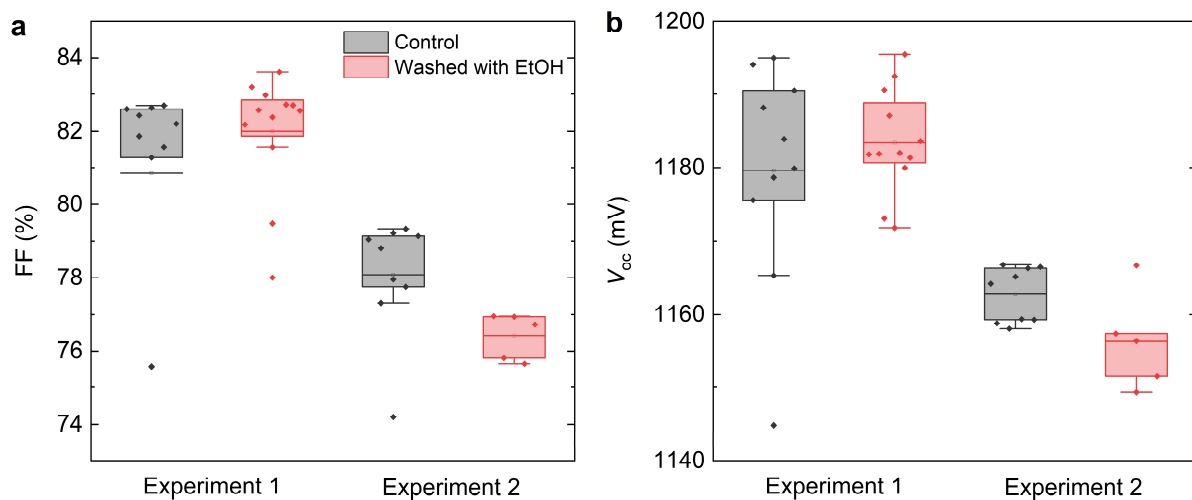
**Fig. S12. Perovskite cells with 2PACz versus Me-4PACz/SiO<sub>2</sub>-NP.** a-d, Fill factor (a), open-circuit voltage (b), pseudo-FF (c) and series resistance near maximum power point ( $R_s$ ) (d) of single-junction 0.1 cm<sup>2</sup> perovskite solar cells fabricated with 2PACz and Me-4PACz/SiO<sub>2</sub>-NPs as hole transport layers. The perovskite precursor contains 5 mM of pFBPA.



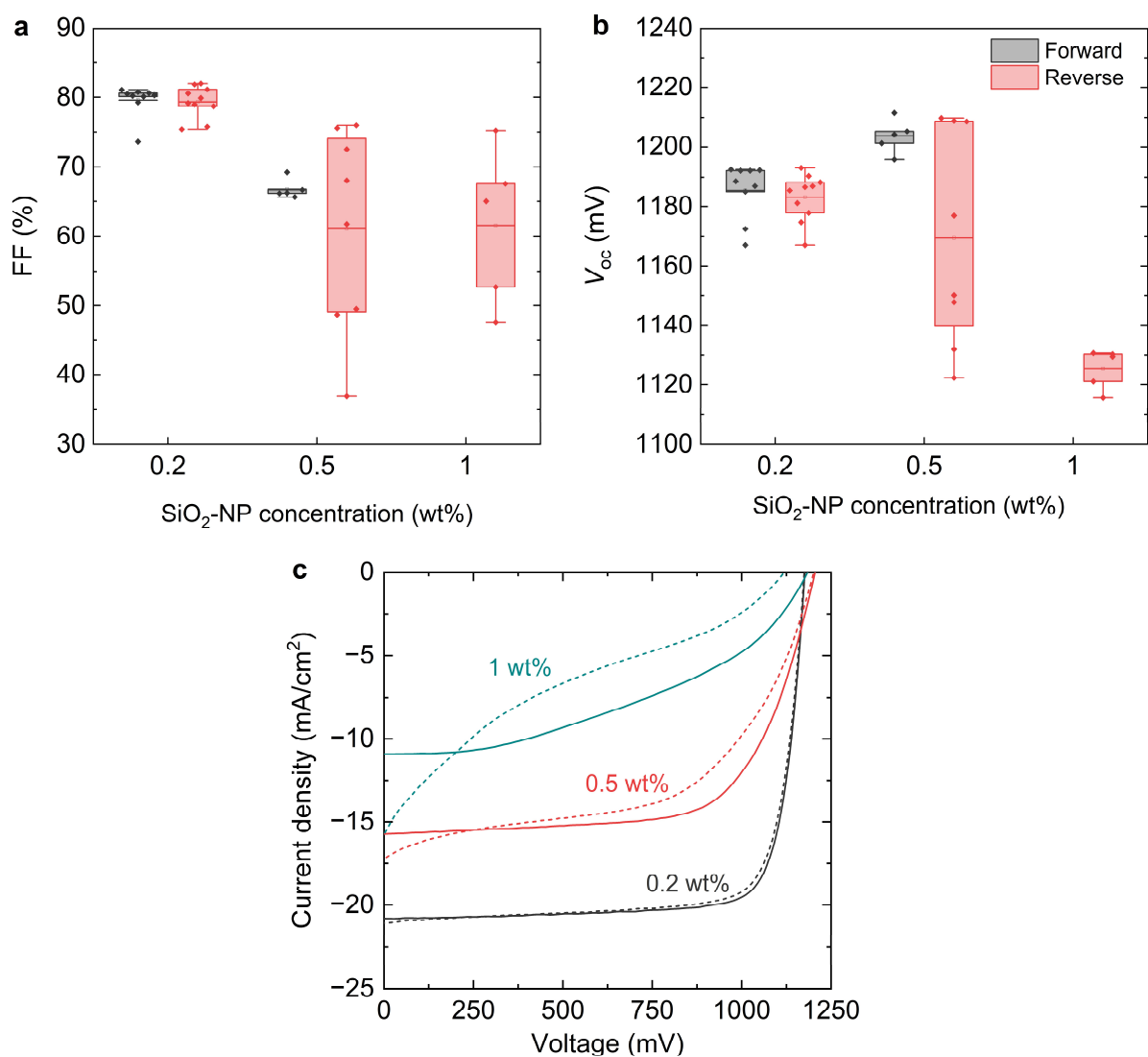
**Fig. S13. Perovskite cells with SiO<sub>2</sub>-NP, without pFBPA.** a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), pseudo-FF (pFF) (c) and series resistance near maximum power-point ( $R_s$ ) (d) of 0.1 cm<sup>2</sup> single-junction perovskite solar cells on glass/ITO/2PACz substrates with varying SiO<sub>2</sub>-NP dispersion concentrations, without pFBPA in the precursor.



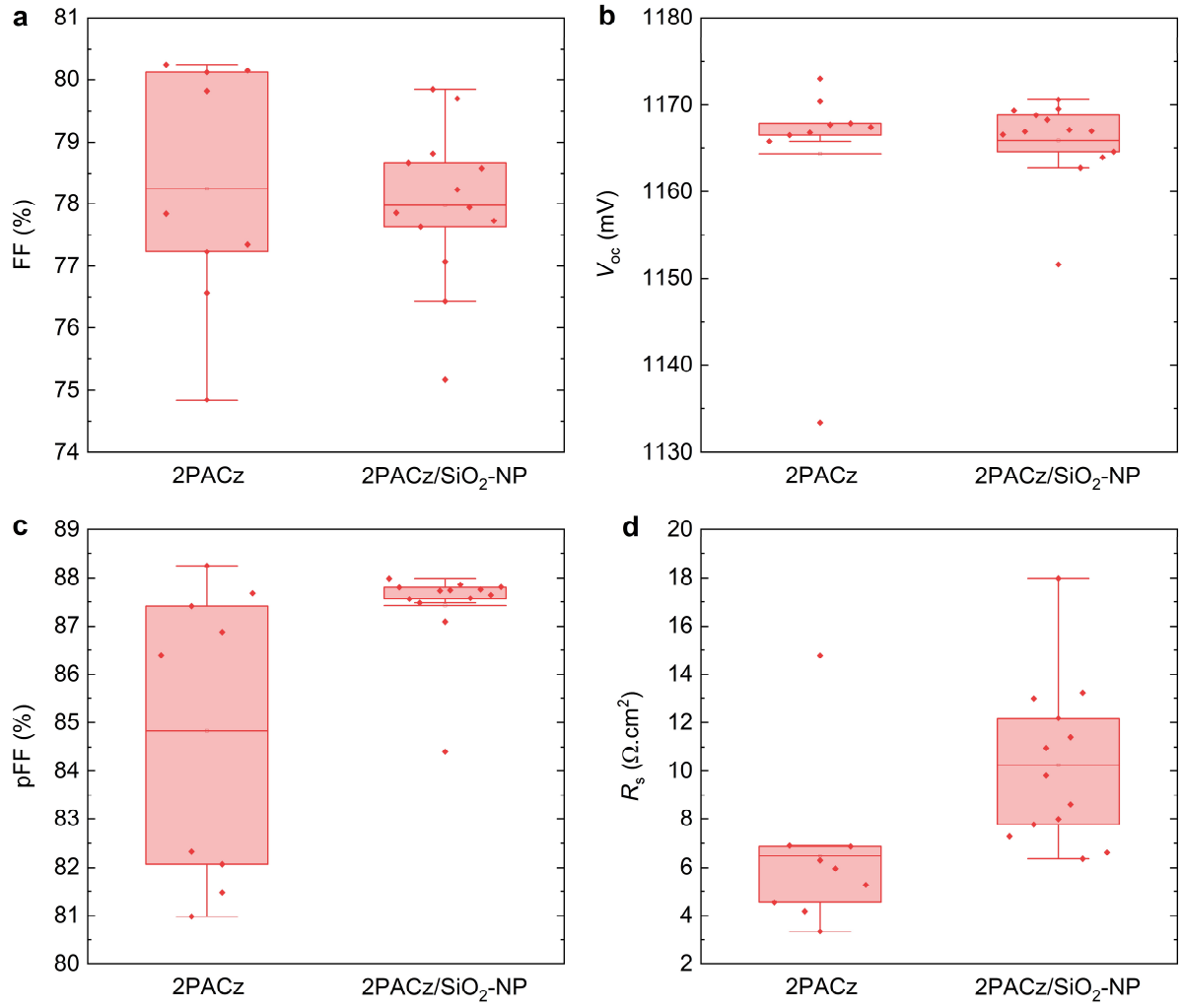
**Fig. S14. Enhancement of shunt resistance by SiO<sub>2</sub>-NPs.** Shunt resistance ( $R_{sh}$ ) versus voltage for 0.1 cm<sup>2</sup> perovskite solar cells with various SiO<sub>2</sub>-NP concentrations measured under dark, assuming  $R_{sh}$  equals to the ratio of terminal voltage and current in the voltage range plotted in the figure. All cells have 2PACz as the hole transport layer and 5 mM pFBPA in the perovskite precursor.



**Fig. S15. Effect of washing 2PACz with ethanol on device performance. a-b,** Fill factor (**a**) and open-circuit voltage ( $V_{oc}$ ) (**b**) of 0.1 cm<sup>2</sup> perovskite solar cells fabricated on glass/ITO/2PACz substrate, with and without a subsequent washing step following the 2PACz deposition. The washing is done by dropping 100  $\mu$ L of ethanol on a sample spinning at 3500 rpm and annealing for 10 min at 100  $^{\circ}$ C on a hot plate. Prior to washing, the 2PACz is coated on the samples and annealed for 10 min at 100 $^{\circ}$ C. The test is repeated in two batch of experiments, labeled as ‘Experiment 1’ and ‘Experiment 2’, with the material configuration and deposition parameters.

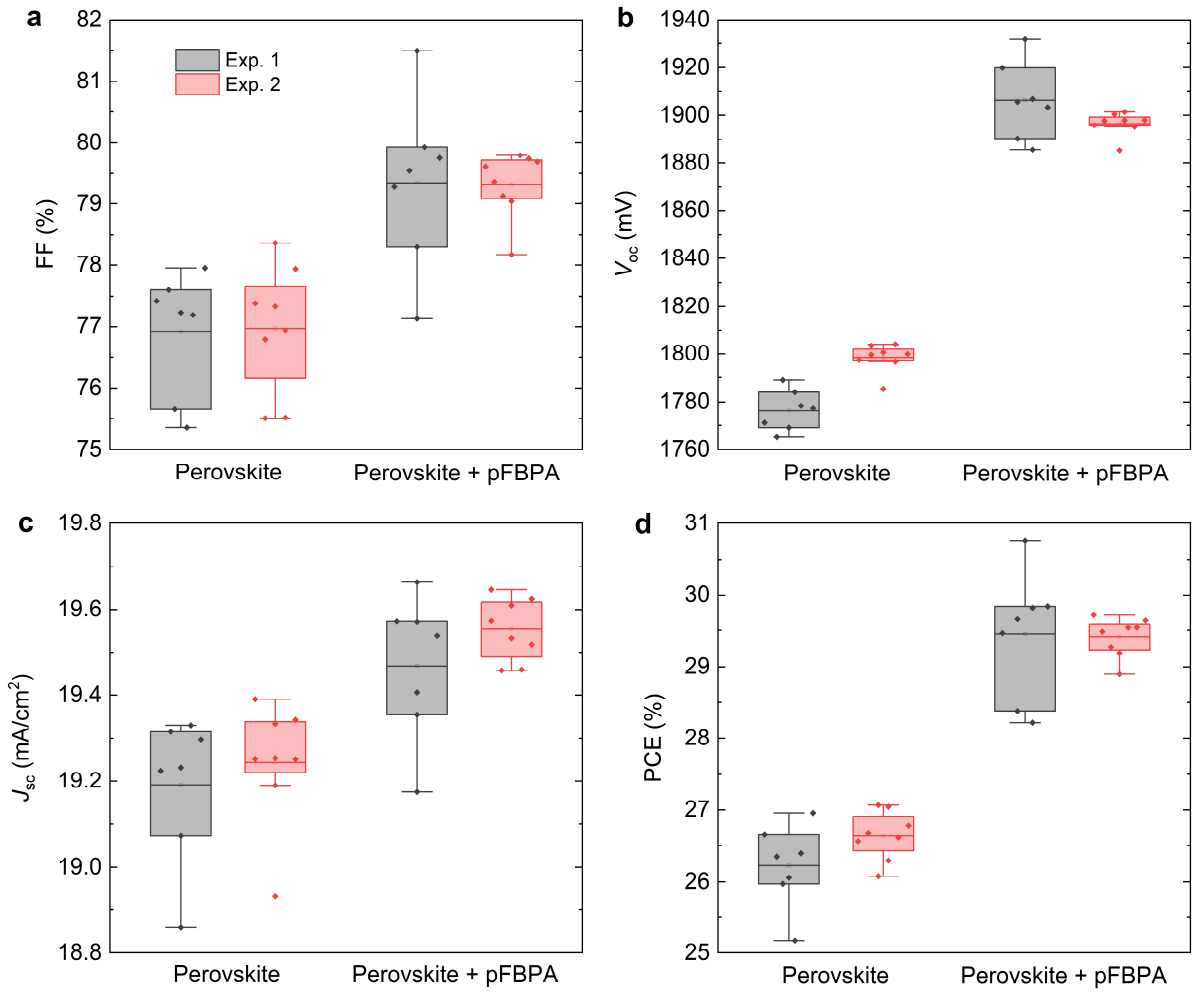


**Fig. S16. Devices with high SiO<sub>2</sub>-NP surface coverage. a-c,** Fill factor (a), open-circuit voltage ( $V_{oc}$ ) (b) and current density versus voltage curves (c) of 0.1 cm<sup>2</sup> perovskite solar cells fabricated on glass/ITO/2PACz/SiO<sub>2</sub>-NP substrates with varying concentrations of SiO<sub>2</sub>-NP dispersion concentrations. Dashed and solid lines show the measurement results of forward (from short-circuit to open-circuit conditions) and reverse scan directions. Scan rate ~0.1V/s.

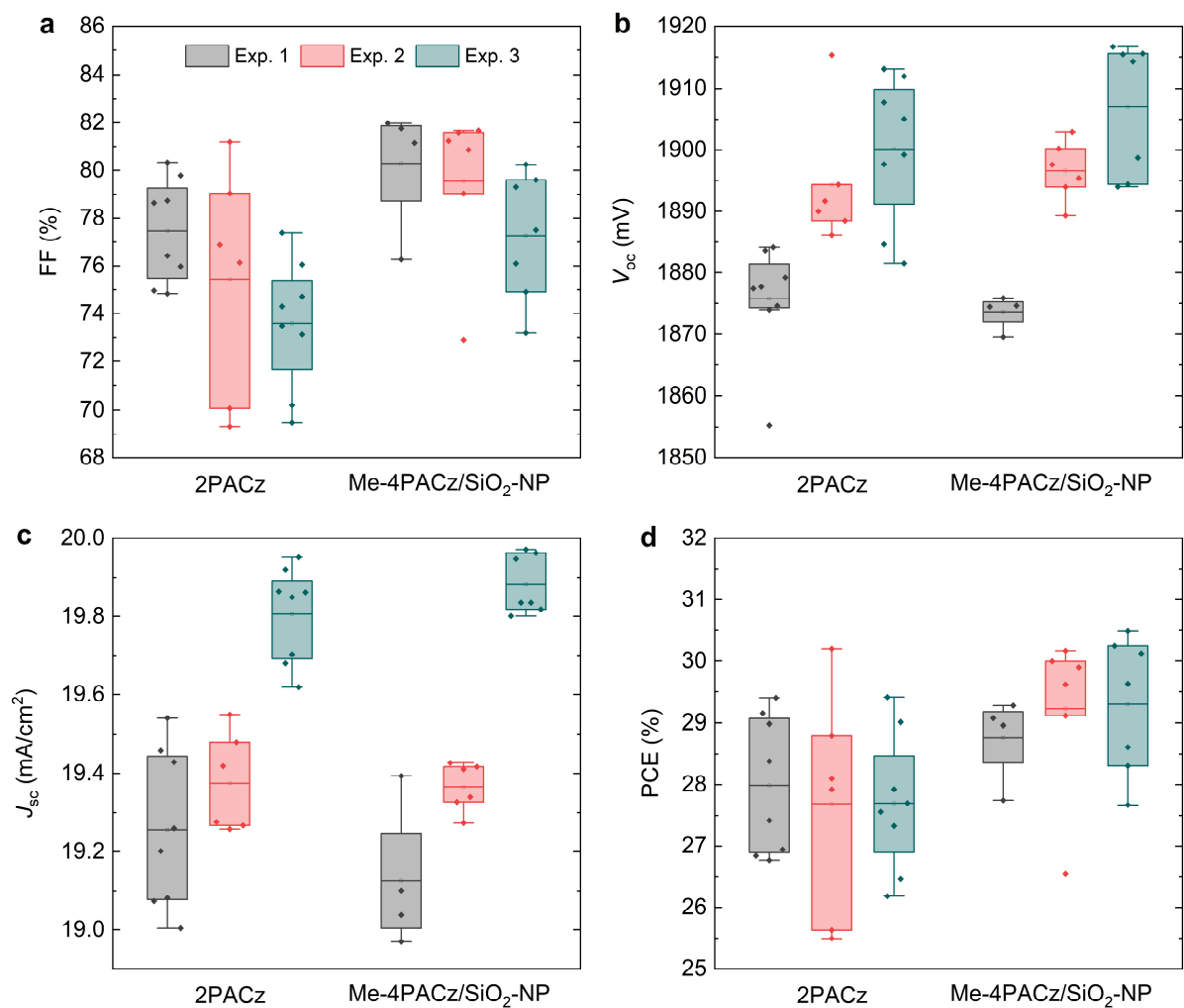


**Fig. S17. Excessive series resistance with 2PACz with SiO<sub>2</sub>-NP.** a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), pseudo-FF (pFF) (c) and series resistance near maximum power point ( $R_s$ ) (d) of single-junction 0.1 cm<sup>2</sup> perovskite solar cells fabricated with on glass/ITO substrates coated with 2PACz or 2PACz/SiO<sub>2</sub>-NP (0.2 wt%).





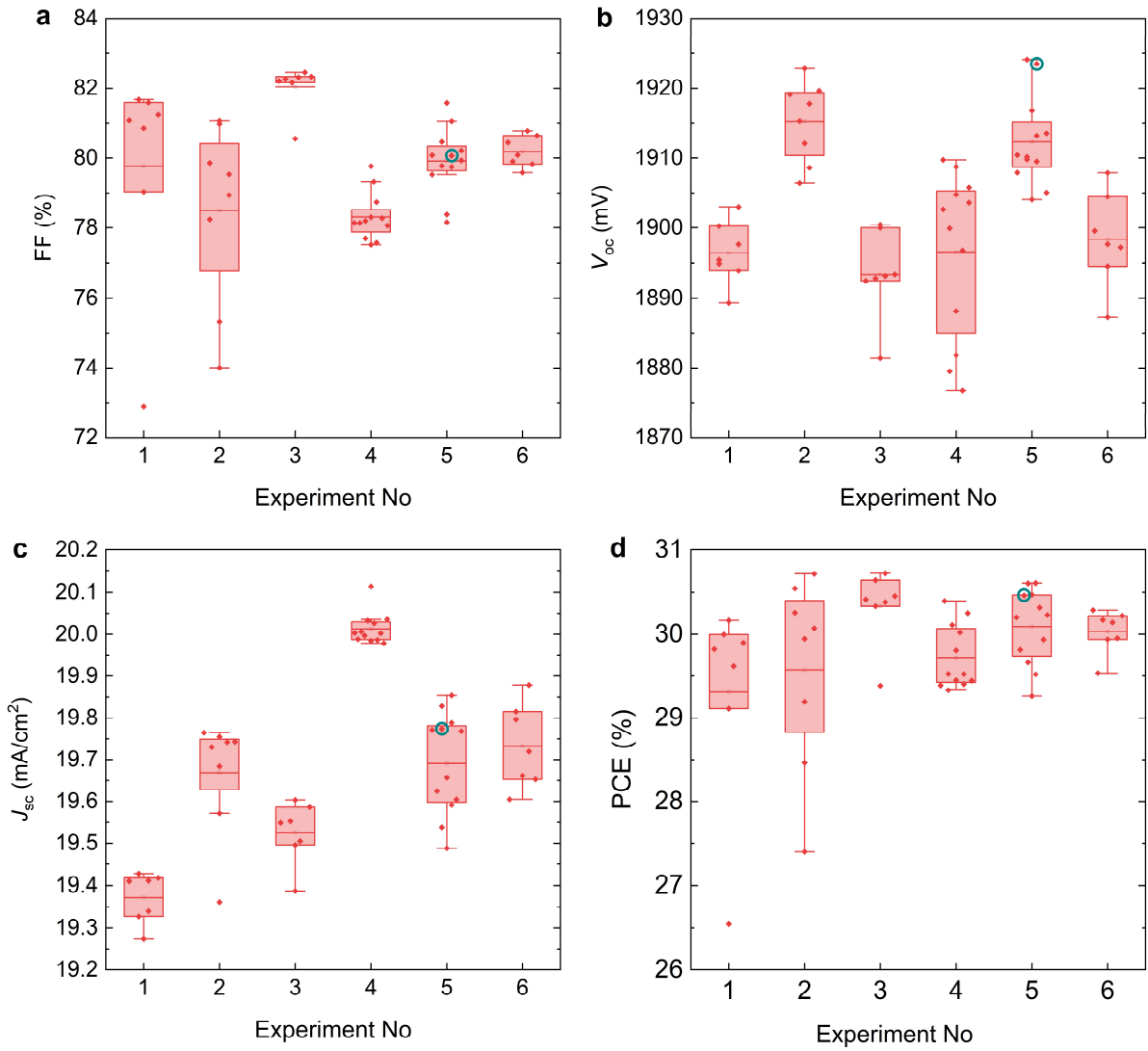
**Fig. S18. Tandem solar cells with and without pFBPA.** a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), short-circuit current density ( $J_{sc}$ ) (c) and power conversion efficiency (PCE) (d) of  $\sim 1$  cm<sup>2</sup> perovskite-Si tandem solar cells without and with 5 mM of pFBPA in the perovskite precursor. The experiment is repeated two times with the same deposition parameters to the best of our knowledge.



**Fig S19. Tandem solar cells with 2PACz versus Me-4PACz/SiO<sub>2</sub>-NP.** a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), short-circuit current density ( $J_{sc}$ ) (c) and power conversion efficiency (PCE) (d) of  $\sim 1$  cm<sup>2</sup> perovskite-Si tandem solar cells with 2PACz and Me-4PACz/SiO<sub>2</sub>-NP. The experiment is repeated three times, with the only intentional difference being in the  $J_{sc}$  mismatch between the perovskite and Si subcells.

**Table S1.** Short-circuit current density ( $J_{sc}$ ) mismatch of the perovskite and Si subcells of the tandem devices shown in Fig. S19.

|              | Average short-circuit current density mismatch $J_{sc,top} - J_{sc,bottom}$ (mA/cm <sup>2</sup> ) |
|--------------|---------------------------------------------------------------------------------------------------|
| Experiment 1 | 0.7                                                                                               |
| Experiment 2 | 0.2                                                                                               |
| Experiment 3 | 0.6                                                                                               |
| Experiment 4 | 0.0                                                                                               |
| Experiment 5 | 0.2                                                                                               |
| Experiment 6 | 0.2                                                                                               |



**Fig. S20.** Tandem cells with both pFBPA and Me-4PACz/SiO<sub>2</sub>-NP fabricated in consecutive batches. a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), short-circuit current density ( $J_{sc}$ ) (c) and power conversion efficiency (PCE) (d) of  $\sim 1$  cm<sup>2</sup> perovskite-Si tandem solar cells with Me-4PACz/SiO<sub>2</sub>-NP and 5 mM of pFBPA in the precursor fabricated in six consecutive batches. The only intentional difference in device configuration is the  $J_{sc}$  mismatch between the perovskite and Si subcells induced by varying the bandgap or the thickness of the perovskite absorber. The measurement results of the tandem cell that had been independently certified (i.e., Fig. 3a) is marked with a green circle.

## EPFL PVLAB/CSEM

### Perovskite/Si Cell

Device ID: 110-1

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Spectrum: ASTM G173 global

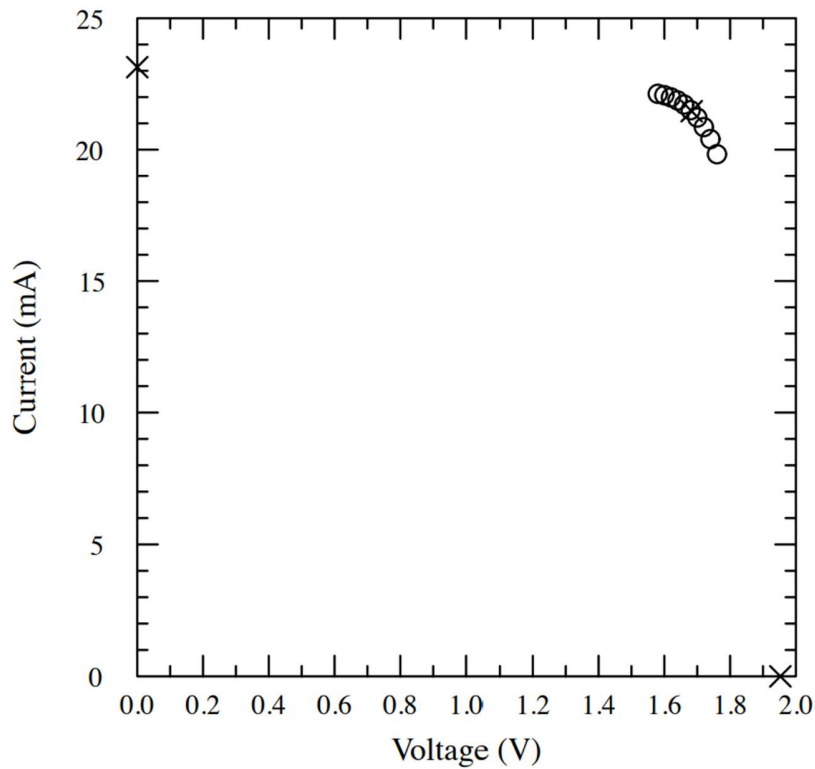
Device temperature:  $24.7 \pm 0.2$  °C

Device area:  $1.1679 \text{ cm}^2 \pm 0.2\%$

Irradiance:  $1000.0 \text{ W/m}^2$



OSMSS IV System  
PV Cell & Module Performance



$$V_{oc} = 1.9528 \text{ V} \pm 0.48\%$$

$$I_{sc} = 23.139 \text{ mA} \pm 0.73\%$$

$$J_{sc} = 19.812 \text{ mA/cm}^2 \pm 0.86\%$$

$$\text{Fill Factor} = (79.9 \pm 1.07) \%$$

$$I_{max} = 21.463 \text{ mA} \pm 0.74\%$$

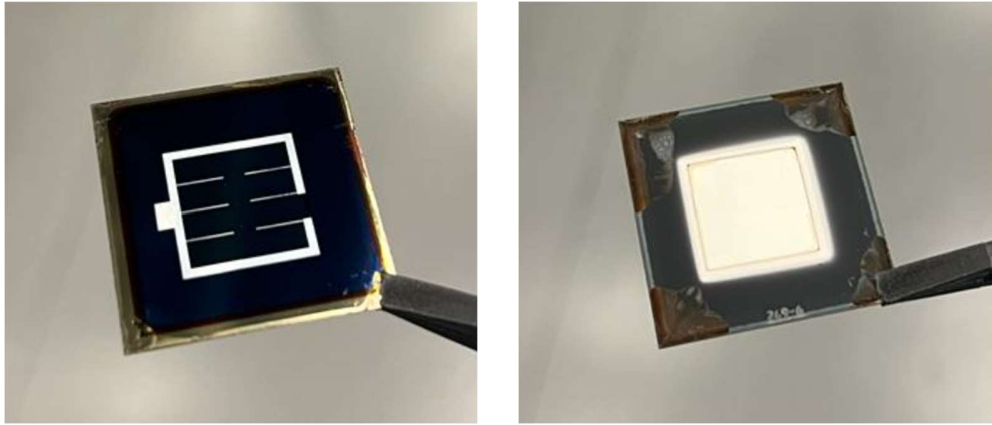
$$V_{max} = 1.6831 \text{ V} \pm 0.70\%$$

$$P_{max} = 36.124 \text{ mW} \pm 0.95\%$$

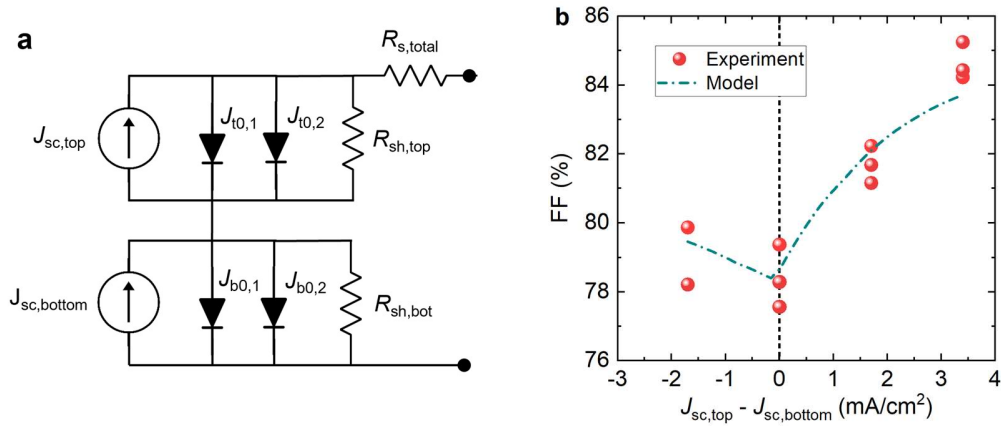
$$\text{Efficiency} = (30.93 \pm 0.29) \%$$

Scan duration: 784 s

**Fig. 21. Certification document of a perovskite-Si tandem cell.** Independently certified by National Renewable Energy Laboratory using the One-Sun Multi-Source Simulator (OSMSS) system and the asymptotic maximum power point scan method.

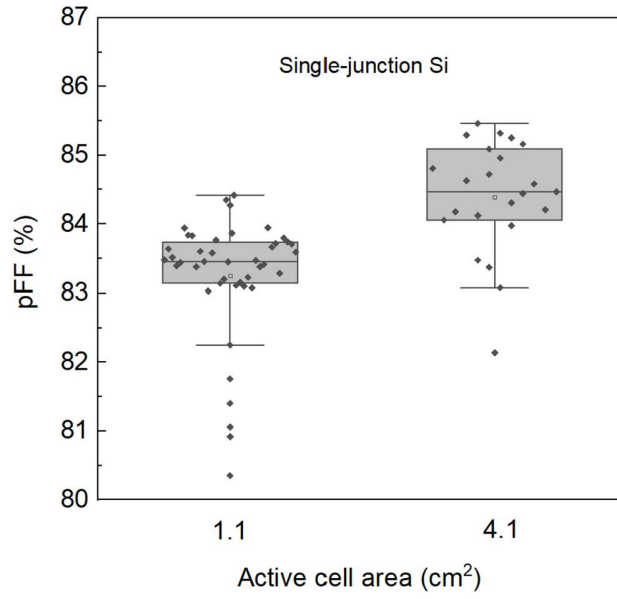


**Fig. S22. Tandem solar cells embedded in  $2.5 \times 2.5 \text{ cm}^2$  Si substrates.** Photographs of the front and rear side of completed perovskite-Si tandem solar cells.

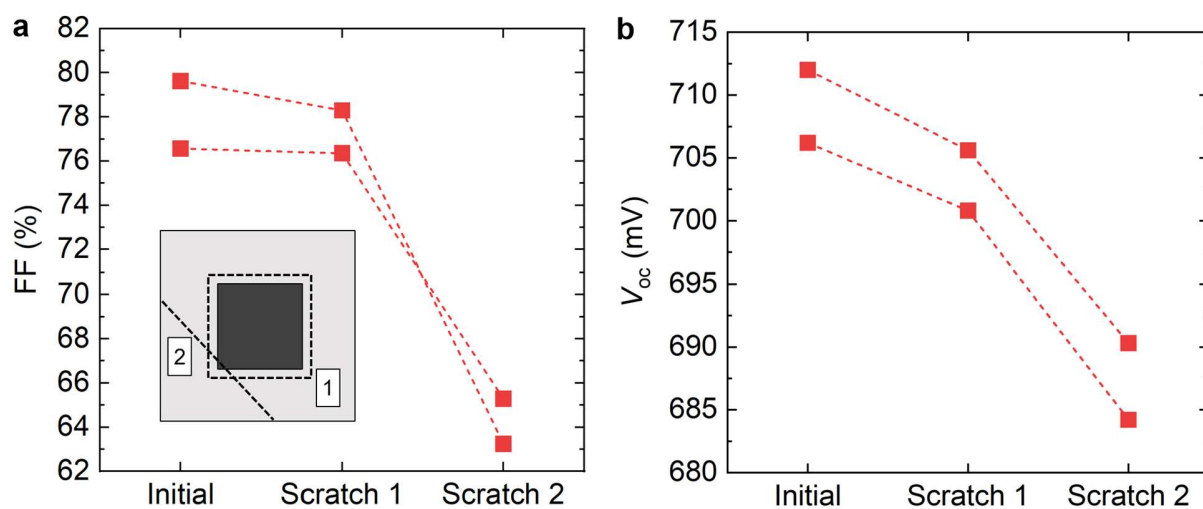


| Parameter                                          | Value                 |
|----------------------------------------------------|-----------------------|
| $J_{sc,top} + J_{sc,bottom}$ (mA/cm <sup>2</sup> ) | 40.5                  |
| $R_{s,total}$ (Ω.cm <sup>2</sup> )                 | 6.0                   |
| $J_{t0,1}$ (A/cm <sup>2</sup> )                    | $5.0 \times 10^{-23}$ |
| $J_{t0,2}$ (A/cm <sup>2</sup> )                    | $7.0 \times 10^{-13}$ |
| $R_{sh,top}$ (Ω.cm <sup>2</sup> )                  | $4.0 \times 10^3$     |
| $J_{b0,1}$ (A/cm <sup>2</sup> )                    | $3.0 \times 10^{-14}$ |
| $J_{b0,2}$ (A/cm <sup>2</sup> )                    | $1.0 \times 10^{-11}$ |
| $R_{sh,bot}$ (Ω.cm <sup>2</sup> )                  | $5.0 \times 10^5$     |

**Fig. S23. Modelling tandem solar cells.** **a**, Equivalent circuit model (ECM) of the perovskite-Si tandem devices with a two-diode model for each of the subcells. **b-c**, Experimental measurement and numerical calculation results of fill factor (FF) versus short-circuit current density of perovskite ( $J_{sc,top}$ ) and Si subcells ( $J_{sc,bottom}$ ) (**b**) and the parameters of the ECM used in the calculations. (**c**). The mismatch conditions are varied by illuminating the cells with ultraviolet (peak intensity at 428 nm) and infrared (peak intensity at 950 nm) light emitting diodes.

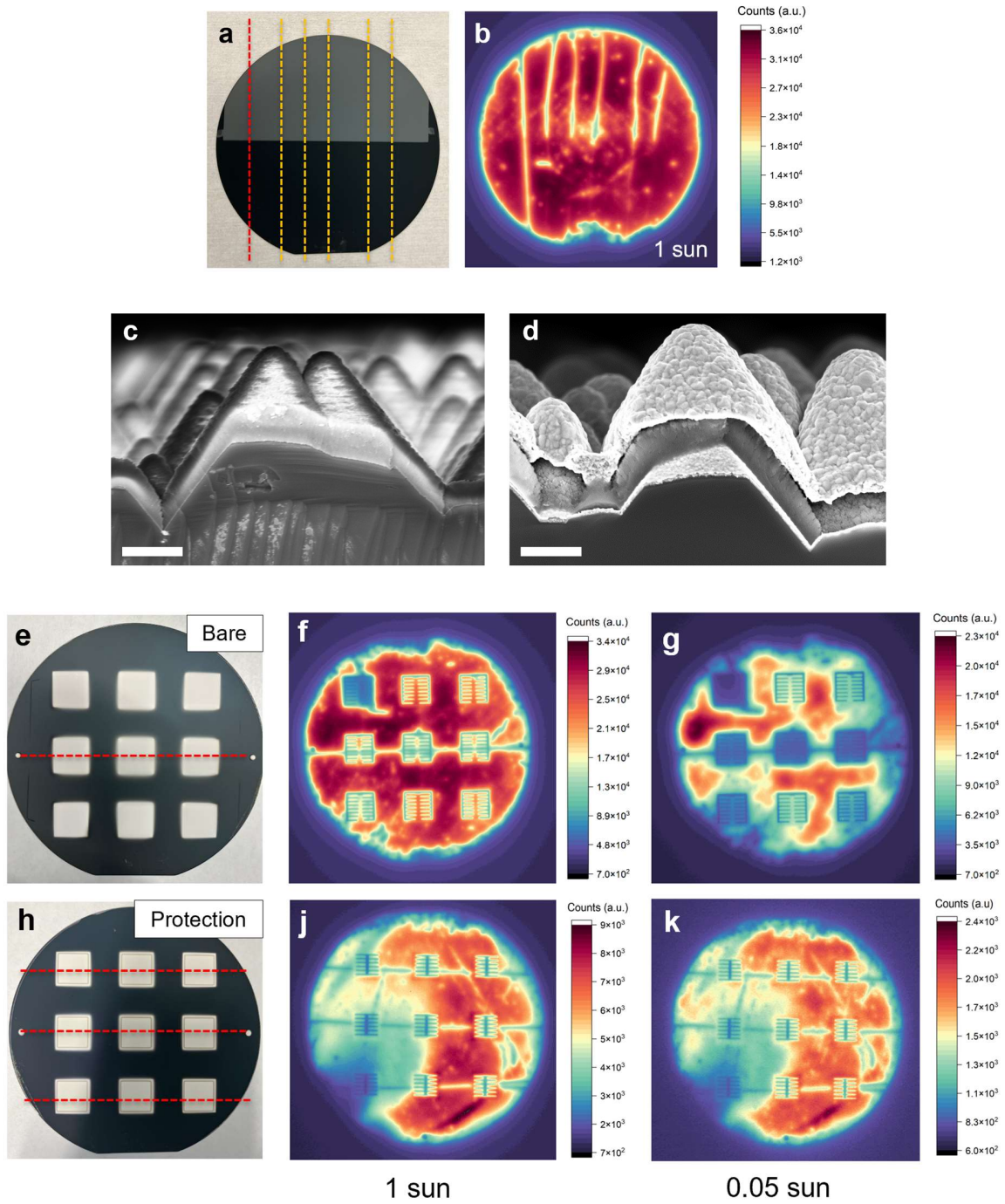


**Fig. S24. Area scaling with Si solar cells.** Pseudo fill factors (pFF) of single-junction Si solar cells with different active cell areas. The 1.1 cm<sup>2</sup> devices were metallized on the front side with a sputtered Ag grid, resulting in a high shadowing fraction and  $J_{sc} \sim 25$  mA/cm<sup>2</sup>. The 4.1 cm<sup>2</sup> cells were metallized at the front side by screen printing Ag with a low shadowing fraction, resulting in a  $J_{sc} \sim 40$  mA/cm<sup>2</sup>.

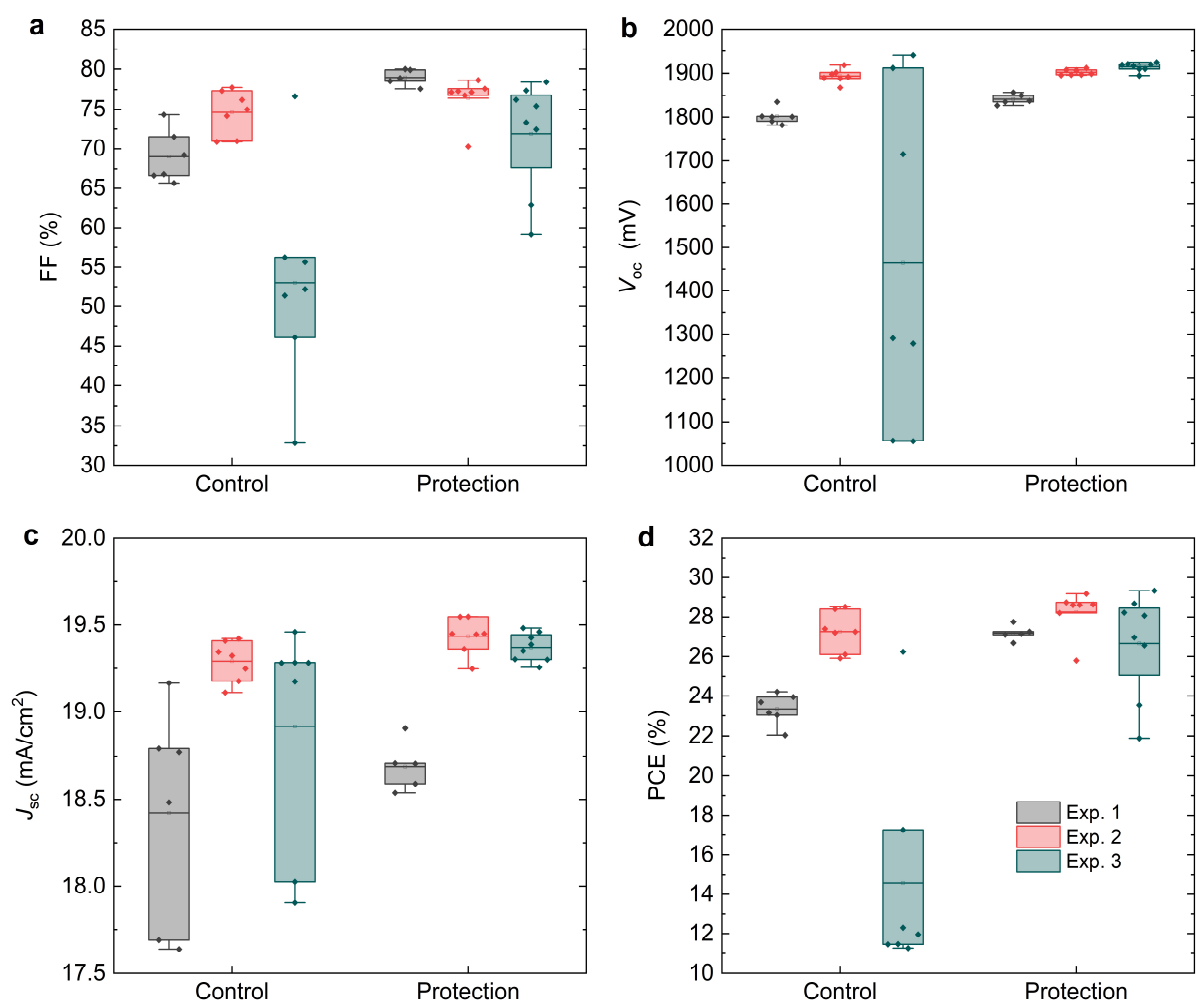


**Fig. S25. Scratch tests of single-junction Si cells. a-b,** Fill factor (FF) (**a**) and open-circuit voltage ( $V_{oc}$ ) (**b**) of two single-junction cells that are scratched with a load-controlled pen (0.1 N.m) with a diamond tip at different locations on the rear side. The ‘Scratch 1’ surrounds the rear Ag contact with a rectangle shape and is spaced 1 mm apart from the contact. The ‘Scratch 2’ passes through both the metallized and non-metallized area and the length of the line crossing the Ag contact is approximately 1.5 mm. The thickness of the Ag layer is ~150 nm.





**Fig. S26. SiO<sub>x</sub> protection for the rear side.** **a-b**, Photograph **(a)** and photoluminescence (PL) measurement image **(b)** of a half-finished c-Si cell, with the thin-film Si depositions completed yet without the TCO or Ag layers. The upper half of the wafer is left bare, while the lower side is coated with a ~500 nm-thick SiO<sub>x</sub> layer. The wafer is scratched on the side with the p-type Si layer, using a load-controlled diamond pen with a load of 0.1 N.m (red dashes) and by sliding a free-standing diamond pen with a weight of X gr (yellow dashes), that induces a load lower than the lower limit of the load-controlled pen. **c-d**, Scanning electron microscope images of a SiO<sub>x</sub> **(c)** and Ag/SiO<sub>x</sub>/Ag contact **(d)**. **e-k**, Photographs and PL images taken at 0.05 and 1-sun of ~1 cm<sup>2</sup> cells embedded in a 4-inch wafer and scratched as indicated by red dashed lines with a load-controlled pen at 0.1 N.m. While the cell in the top row **(e-g)** only has a 150 nm-thick Ag, the cell on the bottom **(h-k)** has a SiO<sub>x</sub>-based rear protection scheme.



**Fig. S27. Tandem solar cells with a rear protection scheme.** a-d, Fill factor (FF) (a), open-circuit voltage ( $V_{oc}$ ) (b), short-circuit current density ( $J_{sc}$ ) (c) and power conversion efficiency (PCE) (d) of  $\sim 1$  cm<sup>2</sup> perovskite-Si tandem solar cells with and without a SiO<sub>x</sub>-based rear protection scheme. The experiment is repeated three times with different top cell configurations at different stages of device development. The ‘Experiment 1’ has a relatively thin and low bandgap top perovskite cell (1.63 eV, 500 nm) and 2PACz as the hole transport layer (HTL), ‘Experiment 2’ and ‘Experiment 3’ have 2PACz and Me-4PACz/SiO<sub>2</sub>-NP as HTLs respectively, and both have similar perovskite absorbers (1.65 eV, 600 nm).