Bottom-up modification boosts the performance of narrow-bandgap lead-tin perovskite single-junction and tandem solar cells

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Experimental section

Materials

Methylammonium iodide (MAI, >99.0%) and formamidinium iodide (FAI, >98.0%) were purchased from GreatCell Solar Materials. Lead (II) iodide (PbI₂) was bought from Tokyo Chemical Industry Co, Ltd. Lead thiocyanate (Pb(SCN)₂, 99.5%), tin(II) fluoride (SnF₂, 99%), cesium \Box iodide (CsI), tin(II) iodide (SnI₂, beads, 99.99%), lead(II) bromide(PbBr₂), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and chlorobenzene (CB) were purchased from Sigma-Aldrich. Glycine hydrochloride (GlyCl) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) solution (AI 4083) was purchased from Heraeus Co, Ltd. Dipropylammonium iodide (PDAI₂) and [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic Acid (MeO-2PACz) were purchased from Tokyo Chemical Industry Co. Ltd. Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Fullerene (C_{60}) were purchased from Xi'an Polymer Light Technology Corp. Bathocuproine (BCP) was obtained from Jilin OLED Material Tech Co., Ltd. Tetrakis(dimethylamino) tin (IV) (99.9999%) for atomic layer deposited (ALD) SnO₂ was bought from Nanjing Ai Mou Yuan Scientific Equipment Co. Ltd. All the materials were used as received without further purification.

Preparation of wide-bandgap perovskite precursors

1.5 M wide-bandgap perovskite precursor solutions with a composition of $FA_{0.75}Cs_{0.25}Pb(I_{0.8}Br_{0.2})_3$ were prepared by dissolving FAI, CsI, PbI₂, and PbBr₂ in a mixed solvent of DMF and DMSO with a volume ratio of 3:1. The precursor solutions were added with 1 mol% KI and then filtered with a 0.22 µm PTFE membrane before use.

Preparation of PEDOT: PSS and IPA precursor solutions containing GlyCl

The precursor solutions of PEDOT: PSS containing glycine were obtained by dissolving 0-15 mg of GlyCl into 1 mL of PEDOT: PSS precursors, and stirring at room temperature for 10 min. The IPA precursor solutions containing GlyCl were obtained by dissolving 0-4 mg of GlyCl into 1 mL of IPA precursors and kept heating on a hot plate at 65°C for 3 hours.

Preparation of narrow-bandgap perovskite precursors

The precursor solutions of 1.8 M FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I₃ were obtained by dissolving

216.72 mg of FAI, 85.8 mg of MAI, 335.3 mg of SnI₂, 414.9 mg of PbI₂, 14.1 mg of SnF₂, and 0-4 mol% of GlyCl in a mixed solvent of 750 μ L of DMF and 250 μ L of DMSO. The mixed solutions were kept for 3 hours before spin-coating in an N₂-filled glove box and then filtered through a 0.22 μ m PTFE membrane before use.

Fabrication of wide-bandgap perovskite solar cells

The pre-patterned ITO substrates were cleaned by sonication with detergent, deionized water, acetone, and ethanol for 15 min sequentially. Before use, the substrates were treated with ultraviolet ozone for 15 min and then transferred into an N₂-filled glovebox. Then, the ITO/glass substrates were spin-coated with a thin layer of a self-assembled monolayer (SAM) MeO-2PACz at 4,000 rpm for 30 s, followed by annealing at 100 °C for 5 min (about 0.3 mg/mL in ethanol). To obtain wide-bandgap perovskite films, the perovskite precursor solutions (30 μ L) were dropped on the substrates and then spin-coated at 500 rpm for 2 s and then at 4000 rpm for 60 s with 300 μ L of diethyl ether dripping at the 36 s of the second step. After that, the as-prepared films were annealed at 100°C for 10 min immediately. Then, 1 mg/mL of PDAI₂ solution (70 μ L) was spin-coated onto the as-prepared perovskite films at 4000 rpm for 30 s and followed by annealing at 100°C for 5 min. In the following, 20 nm of C₆₀ was deposited on the films by thermal evaporation.

For semitransparent cells, 20 nm of ALD SnO_2 was deposited on the C₆₀-coated films. Then, 100 nm of ITO was sputtered at a power of 100 W under an Ar pressure of 2 mTorr.

Fabrication of narrow-bandgap perovskite solar cells

Before film deposition, the pre-patterned ITO substrates were washed by sonication with detergent, deionized water, acetone, and ethanol for 15 min sequentially. The cleaned ITO substrates were treated with UV ozone for 15 min. Then, the filtered PEDOT: PSS solutions were spun cast onto the ITO substrates at 4000 rpm for 30 s and annealed at 140°C for 20 min. In the following, the filtered FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I₃ precursors were deposited on the PEDOT: PSS-coated substrates by a two-step spin-coating process: keeping 1000 rpm for 10 s and then 5000 rpm for 40 s, and dropping

400 μ L of CB during the second spin-coating step at 20 s before the end of the procedure. After that, the as-prepared perovskite films were immediately annealed on a hot plate at 100 °C for 10 min. For GlyCl post-treatment, 60 μ L of GlyHCl IPA solution was spin-coated onto the as-prepared perovskite films at 5000 rpm for 30 s and then annealed at 95°C for 5 min. In the final, C₆₀(20 nm)/BCP(7 nm)/Cu(80 nm) were sequentially deposited on the substrates by thermal evaporation under a vacuum pressure of 5.0×10⁻⁴ Pa.

For the space-charge-limited current (SCLC) measurements^{1, 2}, hole-only devices were fabricated. Briefly, a P3HT solution (10 mg/mL in CB, doped with 10 wt% Tris(2,4-pentanedionato)gallium) was spun cast onto perovskite films on PEDOT: PSS-coated substrates at 3000 rpm for 20 s. In the following, 80 nm of Au was thermally evaporated on the substrates to complete the fabrication.

Characterizations

Absorption spectra were measured by a UV-visible spectrophotometer (SHIMADZU mini 1280). Crystal structure and phase of perovskite films were characterized by an X-ray diffraction instrument (Bruker AXS, D8 Advance). Scanning electron microscope (SEM) images of perovskite films and devices were obtained with a Zeiss SIGMA field emission SEM. Steady-state PL measurements of perovskite films were recorded by a DeltaFlex fluorescence spectrometer (HORIBA) with a 481 nm picosecond pulsed diode laser. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) images of perovskite films were obtained by a Bruker Dimension Icon in a Scanasyst-Air and Peak force KPFM Mode. X-ray photoelectron spectroscopy (XPS) measurements were carried out by an ESCALAB 250Xi (Thermo Scientific, ESCLAB 250Xi, USA). XPS spectra were fitted using a Thermo Avantage software. Preceding the fitting process, energy levels were meticulously calibrated, with the reference C1s level set at 284.6 eV. When fitting the tin peaks, the full widths at half-maximum of Sn, Sn²⁺, and Sn⁴⁺ were consistently aligned. Moreover, in light of the observed shifts in XPS spectra upon GlyCl doping, we endeavored to

sustain a fixed separation between Sn, Sn²⁺, and Sn⁴⁺ peaks across all curves, in order to best accommodate the total Sn curves. Finally, the Thermo Advantage software automatically calculated the area ratios of Sn²⁺ and Sn⁴⁺ by integrating the respective peak areas. Fourier transform infrared spectroscopy (FTIR) spectra were obtained by a NICOLET 5700 FTIR Spectrometer with a wavenumber range from 900 to 4000 cm⁻¹. Current density-voltage (J–V) curves, space-charge-limited current (SCLC), and steady-state power output (SPO) measurements were performed using a Keithley 2400 source meter under standard AM 1.5 G illumination using a solar simulator (Enlitech, SS-F5-3A). J-V measurements for narrow-bandgap solar cells were scanned from 1.0 to -0.1 V and then reversed again from -0.1 to 1.0 V. J-V measurements for wide-bandgap solar cells were scanned from 1.3 to -0.1 V and then reversed again from -0.1 to 1.3 V. The active region (0.0948 cm²) of the devices was covered by a mask with an aperture area of 0.070225 cm². EQE spectra were collected using a QE system (Enli Technology Co., Ltd). Electrochemical impedance spectra (EIS) and Mott-Schottky spectra were recorded on a CHI 760E electrochemical workstation (Shanghai Chenhua Instruments, China). EIS measurements were conducted in a dark environment with bias voltages set to 0V. For the performance measurements of 4terminal tandem solar cells, J-V curves, SPO efficiencies, and EQE spectra of narrow-bandgap bottom cells were taken by using a semitransparent wide-bandgap top cell as the optical filter. J-V curves for filtered narrow-bandgap solar cells were performed by scanning from -0.1 to 1.0 V and then reversed again from 1.0 to -0.1 V with a voltage step of 20 mV and a delay time of 50 ms.



Figure S1. (a) Bandgaps of a pristine Pb-Sn perovskite film (control) and Pb-Sn perovskite films with bottom, bottom/body, and bottom/body/top GlyCl modifications.



Figure S2. Zoomed-in XRD patterns of a neat $FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I_3$ film, $FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I_3$ films with bottom, bottom/body, and bottom/body/top GlyCl modifications.



Figure S3. SEM images of (a) a control, (b) a bottom, (c) a bottom/body, and (d) a bottom/body/top GlyCl-modified perovskite films deposited on PEDOT-coated ITO substrates.



Figure S4. AFM images of (a) a control, (b) a target GlyCl-modified perovskite films deposited on PEDOT-coated ITO substrates.



Figure S5. KPFM images of (a) a control (b) a target GlyCl-modified perovskite films deposited on PEDOT-coated ITO substrates.



Figure S6. KPFM images of PEDOT:PSS films (a) without and (b) with GlyCl addition, and (c) a highly oriented pyrolytic graphite (HOPG) as a standard sample $(E_f=4.50 \text{ eV})$.



Figure S7. Photograph of perovskite precursor solutions without (the left one) and with GlyHCl addition (the right one) in ambient air for one week.



Figure S8. A cross-sectional SEM image of a representative GlyCl-incorporated PSC.



Figure S9. (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCEs of PSCs introducing different concentrations (0-15 mg/mL) of GlyCl into PEDOT: PSS solutions.



Figure S10. (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCEs of PSCs introducing different concentrations (0-4 mol%) of GlyCl into perovskite precursors.



Figure S11. (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCEs of PSCs introducing different concentrations (0-4 mg/mL in IPA) of GlyCl by post-coating on top of perovskite layers.



Figure S12. Statistics of PCE distribution of twenty control PSCs and twenty target PSCs with bottom/body/top GlyCl modifications.



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====Measurement Results ====

	Forward Scan (Isc to Voc)		Reverse Scan	
			(Voc to lsc)	
Area		6.9	92 mm²	
lsc	1.444 m/	4	1.445	mA
Voc	1.238 V		1.240	v
Pmax	1.484 m ¹	N	1.491	mW
lpm	1.362 m/	4	1.366	mA
Vpm	1.090 V		1.092	v
FF	83.06 %		83.21	%
Eff	21.45 %		21.55	%

- Spectral Mismatch Factor SMM=1.0038.

- Designated illumination area defined by a thin metal mask was measured by a measuring microscope.

No temperature control during MPP-Tracking.

- Test results listed in this measurement report refer exclusively to the mentioned measured sample.





Figure S13. Certified results of an opaque wide-bandgap perovskite solar cell, measured by Shanghai Institute of Microsystem and Information Technology (*SIMIT*).

Condition	Scan mode	V _{OC}	$J_{ m SC}$	FF	PCE
		(V)	$(mA cm^{-2})$	(%)	(%)
Control	Forward	0.75	29.17	64.70	14.23
	Reverse	0.77	29.17	66.90	14.28
Bottom	Forward	0.78	28.80	68.63	15.46
	Reverse	0.79	29.00	72.33	16.51
Bottom/body	Forward	0.82	29.41	74.44	17.86
	Reverse	0.82	29.48	75.62	18.30
Bottom/body/top	Forward	0.85	30.17	76.72	19.73
	Reverse	0.86	30.16	78.07	20.19

Table S1. Photovoltaic performance of mixed Pb–Sn PSCs with different modification methods.

Table S2. Photovoltaic performance of a semitransparent wide-bandgap top cell and a filtered narrow-bandgap multi-GlyCl-modified bottom cell.

Condition	Scan mode	V _{OC} (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)
WBG	Forward	1.22	19.49	82.55	19.63
	Reverse	1.22	19.55	82.97	19.82
Filtered NBG	Forward	0.80	11.32	77.91	7.11
	Reverse	0.80	11.34	78.44	7.25
4-terminal	Forward	-	-	-	26.74
	Reverse	-	-	-	27.07

References

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