Supporting Information

for Adv. Funct. Mater., DOI: 10.1002/adfm.202107650

Sn-Pb Mixed Perovskites with Fullerene-Derivative Interlayers for Efficient Four-Terminal All-Perovskite Tandem Solar Cells

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1. Experimental Section

Preparation of narrow-bandgap (NBG) perovskite precursor

The Cs$_{0.025}$(FA$_{0.83}$MA$_{0.17}$)$_{0.975}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite precursor was prepared by dissolving 0.85 M tin iodide (SnI$_2$, Alfa Aesar, 99.999%), 0.85 M lead iodide (PbI$_2$, TCI), 1.36 M formamidinium iodide (FAI, GreatCell Solar), 0.34 M methylammonium iodide (MAI, GreatCell Solar), 0.01 M lead thiocyanate (Pb(SCN)$_2$, Sigma Aldrich, 99.5%), and 0.057 M tin fluoride (SnF$_2$, Sigma Aldrich, 99%) in a 9:1 (by volume) mixture solvent of dimethylformamide (DMF, Sigma Aldrich, anhydrous, 99.8%) and dimethyl sulfoxide (DMSO, Sigma Aldrich, anhydrous, ≥99.9%), and then a 21.8-μl cesium iodide (CsI, Alpha Aesar) solution (1.5 M stock solution in DMSO) was added to achieve the desired perovskite precursor solution. The solution was prepared in a N$_2$ glovebox (O$_2$ < 0.2 ppm and H$_2$O < 0.4 ppm).

Preparation of wide-bandgap (WBG) perovskite precursor

The Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite precursor was prepared by dissolving 0.2 M lead bromide (PbBr$_2$, TCI), 1.1 M PbI$_2$, 1 M FAI, 0.2 M methylammonium bromide (MABr, GreatCell Solar) in a 4:1 (by volume) mixture solvent of DMF and DMSO, and then an 88.9 μl-CsI solution (1.5 M stock solution in DMSO) was added to achieve the desired perovskite precursor solution.

Fabrication of NBG PSCs

The NBG PSCs were fabricated in a planar architecture with the stack of glass/indium tin oxide (ITO)/poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)/Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$/fullerene (C$_{60}$)/fullerene derivatives/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)/silver (Ag). The ITO-coated glass substrates (120 nm, sheet resistance 15 Ω sq$^{-1}$, Luminescence Technology) were cleaned ultrasonically by
deionized water, acetone, and isopropanol for 10 min, respectively. Before use, the substrates were treated by an oxygen plasma for 3 min. A thin PTAA (1.5 mg mL\(^{-1}\) in toluene, \(M_n=17,800\) g/mol, EM INDEX) hole transport layer (HTL) was deposited on cleaned ITO substrates by spin coating at 4000 rpm for 30 s, followed by annealing at 100 °C for 10 min. In accordance with other reports,\(^{[1–3]}\) wetting issues of the perovskite precursor solution on PTAA layer is complicated. Thus, before the deposition of perovskite thin films, 70 µl DMF was first used to treat PTAA layer by spin-coating and then annealing at 100 °C for 2 min to improve the wettability. After that, NBG perovskite thin films were fabricated by vacuum-assisted growth control (VAGC) method: the PTAA-coated substrates were deposited by spin-coating at 5000 rpm for 10 s, and then directly transferred into a vacuum chamber (~10 Pa, with a 150 mL volume size). The optimized time of vacuum exposure is 10 s. The wet perovskite thin films were annealed at 100 °C for 7 min. The whole process of perovskite deposition was conducted in a N\(_2\) glovebox (O\(_2\) < 0.2 ppm and H\(_2\)O < 0.4 ppm). Sequentially, different fullerene derivatives (5 mg mL\(^{-1}\) in 1,2-dichlorobenzene (Sigma Aldrich, anhydrous, 99%)) of phenyl-C61-butryic acid methyl ester (PCBM, Sigma Aldrich, 99%), indene-C60-propionic acid butyl ester (IPB, Solenne BV., >99%), and indene-C60-propionic acid hexyl ester (IPH, Solenne BV., >99%) were deposited on top of the perovskite thin films by spin-coating at 2000 rpm for 60 s. Finally, ~25-nm C\(_{60}\) (Sigma Aldrich, 99.5%), ~3-nm BCP (Luminescence Technology), and ~100-nm Ag were thermally evaporated to complete the devices. The active area of PSCs was 0.105 cm\(^2\).

Fabrication of semitransparent WBG PSCs

The semitransparent WBG PSCs were fabricated in a planar architecture with a device configuration of glass/hydrogen-doped indium oxide In\(_2\)O\(_3\):H (IOH)/SnO\(_2\) nanoparticles/CsFAMAPbIBr/2,2',7,7'-tetrakis[N,N-di(4-methox-yphenyl)amino]-9,9'-spirobifluorene (spiro-MeOTAD)/molybdenum oxide (MoO\(_x\))/indium zinc oxide
(IZO)/magnesium fluoride (MgF₂). SnO₂ nanoparticles (Alfa Aesar, diluted by deionized water to 2% volume ratio) were spin-coated on top of cleaned and plasma-treated IOH-coated glass substrates (230 nm, sheet resistance 23 Ω sq⁻¹, in-house sputtered substrates) at 4000 rpm for 30 s, followed by an annealing at 200 °C for 30 min in air. WBG perovskite thin films were spin-coated in two steps: (1) 1000 rpm for 10 s and (2) 6000 rpm for 20 s. 100 µl of chlorobenzene (CB) was spin-coated dynamically 10 s prior to the end of the second step. The samples were then annealed at 100 °C for 1 h in the glovebox. For preparing the precursor of HTL, 80 mg spiro-MeOTAD (Luminescence Technology) was dissolved in 1 ml of CB with 17.5 µL of a lithium salt solution (520 mg mL⁻¹ of lithium bis(trifluoromethanesulfonyl) imide in acetonitrile) and 28.5 µL of 4-tetra-butylpyridine. The HTL layer was deposited by spin coating at 4000 rpm for 30 s, followed by overnight oxygen doping in a dry box. A 10-nm MoOₓ buffer layer was subsequently thermally evaporated on top of spiro-MeOTAD layer. Finally, a 165-nm IZO and a 165-nm MgF₂ layers were deposited sequentially at the end and serve as the rear electrode and antireflection layer, respectively.

Current-Density–Voltage (J–V) Measurements

The J–V characteristics of all PSCs were measured by a sourcemeter (Keithley 2400) equipped with a xenon lamp based solar simulator (Newport Oriel Sol3A) at AM 1.5G (1000 W m⁻²) irradiation. The scan rate was set to 0.6 V s⁻¹ and the solar simulator was calibrated with a certified Si reference solar cell (KG0, Newport). The stabilized power conversion efficiency (SPCE) was determined by tracking the maximum power point (MPP) under continuous AM 1.5G irradiation. The temperature of all cells was controlled at 25 °C by employing a Peltier element connected to a microcontroller while measuring J–V and MPP.

External quantum efficiency measurements (EQE) and optical characterization
The EQE of and optical spectra for the devices, perovskite and fullerene thin films were measured by Bentham PVE300 system located in a N₂ filled glovebox. EQE measurements applied a chopping frequency of 575 Hz with an integration time of 500 ms.

**Ultraviolet photoelectron spectroscopy (UPS) measurements**

UPS measurements for the perovskite and different fullerene thin films were performed on a Thermo Scientific Escalab 250Xi using He I (21.2 eV) source. The UPS spectra were recorded with a sample bias of -3 V (except -2 V for perovskite sample). Energy resolution was approximately 150 meV for an electron analyzer pass energy of 4 eV. The base pressure of the analysis chamber was better than 10⁻¹⁰ mbar before UPS measurements. The UPS data analysis is down as follow.

Fermi levels of NBG perovskite and fullerenes is calculated according to the following equation:[⁴, ⁵]

\[
WF = E_{\text{vac}} - E_f 
\]  

(S1)

\[
WF = h\nu - (E_{\text{cut-off}} - E_{\text{f-spectrometer}}) 
\]  

(S2)

where \(WF\) is the work function, \(E_f\) is the Fermi level, \(E_{\text{cut-off}}\) is the cut-off binding energy at the secondary electron region, \(E_{\text{vac}}\) is the vacuum energy level (i.e., zero kinetic energy with respect to the sample surface), and \(h\nu\) is the emission energy of the source (Helium irradiation 21.2 eV). The position of \(E_{\text{f-spectrometer}}\) was determined using a sputter-cleaned silver sample.

The \(E_{\text{cut-off}}\) of pristine perovskite, \(C_{60}\), PCBM, IPB and IPH are 16.3, 16.5, 16.6, 16.7, and 16.7 eV, respectively (Figure 2a and S5a). Thus, the corresponding \(WF\) with respect to the \(E_{\text{vac}}\), were calculated to be -4.9, -4.7, -4.6, -4.5, and -4.5 eV, respectively (Figure 2b). The highest occupied molecular orbital (HOMO) or valence band maximum (\(E_{\text{VBM}}\)) can be calculated by HOMO (\(E_{\text{VBM}}\)) = \(E_f - E_{\text{onset}}\), where \(E_{\text{onset}}\) is the binding energy at the frontier electronic structure region. The \(E_{\text{onset}}\) of pristine perovskite, \(C_{60}\), PCBM, IPB and IPH are 0.4, 1.6, 1.4, 1.4, and 1.4 eV, respectively (Figure 2a and S5a). Therefore, the corresponding
HOMO or $E_{\text{VBM}}$ were calculated to be -5.3, -6.3, -6.0, -5.9, and -5.9 eV referenced to the $E_{\text{vac}}$, respectively (Figure 2b). The band gaps ($E_g$) for pristine perovskite, C$_{60}$, PCBM, IPB and IPH estimated from Tauc-plots are 1.26, 1.90, 2.03, 2.07, and 2.07, respectively (Figure S5e-5f). The corresponding lowest unoccupied molecular orbital (LUMO) or conduction band minimum ($E_{\text{CBM}}$) can be calculated ($\text{LUMO} = \text{HOMO} + E_g$, $E_{\text{CBM}} = E_{\text{VBM}} + E_g$) to be -4.0, -4.4, -4.0, -3.8, and -3.8, respectively (Figure 2b).

**X-ray photoelectron spectroscopy (XPS) measurements**

XPS measurements on perovskite samples with and w/o interlayers were conducted by a K-Alpha instrument (Thermo Fisher Scientific) with a monochromatic Al-Kα X-ray source (1486.6 eV) and 400 μm spot size. The samples were measured without applying charge neutralizer system as they were well conducting. Data acquisition and processing were carried out using the Thermo Avantage software. The binding energies are given with respect to that of the C 1s peak of hydrocarbons at 285.0 eV. The spectra were fitted with one or more Voigt profiles. The analyzer transmission function, Scofield sensitivity factors and effective attenuation lengths (EALs) for photoelectrons were applied for quantification.$^6$ EALs were calculated using the standard TPP-2M formalism.$^7$

**Time-resolved photoluminescence (TRPL) spectroscopy**

TRPL measurements were conducted by employing a streak camera system (Hamamatsu Universal Streak Camera C10910) coupled with a spectrometer (Acton SpectraPro SP2300). A 1000 ns time window and a full width at half maximum (FWHM) of the instrumental response function of 90 ns were used in single sweep mode. The second harmonic of a pulsed DPSS laser (Picolo-AOT MOPA, InnoLas Laser) with a pulse width of 1 ns and a repetition rate of 1 kHz was used for the excitation. The excitation was at 532nm with a fluence of 700 nJ cm$^{-2}$. 

6
Steady-state photoluminescence (PL) spectroscopy

Steady-state PL measurements were performed on the FLSP920 Fluorescence Spectrometers (Edinburgh Instruments Ltd.) equipped with a Hamamatsu R2658P photomultiplier. A 635nm LED (PDL-800D, PicoQuant) was employed to supply the excitation light.

Dark J–V curves and ideality factor measurements

The dark J–V curves and light intensity dependence of $V_{OC}$ were performed by Paios (Fluxim AG) system with a white light emitting diode (Cree XP-G). $V_{OC}$ can be estimated by the following equation:[8]

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_t}{J_0} + 1\right)$$

(S3)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the elementary charge, $J_t$ is the theory of current density, and $J_0$ is the reverse saturation current density. $J_0$ can be obtained by the intercept at zero voltage of the linear regression from region B (Figure S1), which is $2.82 \times 10^{-8}$ mA cm$^{-2}$ and $1.23 \times 10^{-7}$ mA cm$^{-2}$ for the devices with and w/o IPH-interlayer.

The effect of interfacial defects within the PSCs was further investigated by tracing the changes of light intensity-dependent $V_{OC}$ (Figure 3d). Logarithmic $V_{OC}$ can be linear fitted by the equation:[9]

$$\frac{\partial V_{OC}}{\partial (ln I)} = \frac{n_{id}kT}{q}$$

(S4)

where $n_{id}$ is the ideality factor, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the elementary charge, and $I$ is the light intensity. The $n_{id}$ values are reflected in the curve slopes.

Electrical impedance spectroscopy (EIS)
EIS for the devices was conducted by Paios system in the dark at the range of 1–2 MHz with a bias of 0 V and amplitude of 70 mV. Nyquist plots were fitted by Z-View program. The impedance spectra at short-circuit condition shown in Figure 3e depict large semicircles in the Nyquist plots, since the small semicircle in the high-frequency region is negligible, see Figure S12a. Generally, the arc at high-frequency presents the signature of the charge transport resistance \( R_{ct} \), and the low-frequency arc is related to the charge recombination resistance \( R_{rec} \) at the perovskite/ETL interfaces.[10–12] In this work, based on the same \( p-i-n \) configuration for all devices, the values of \( R_{ct} \) are expected to be similar and we focus on the comparison of \( R_{rec} \).

Space-charge-limited current (SCLC) method

The SCLC method was conducted on the electron-only devices (ITO/CsFAMAPbSnI/fullerene derivatives (with or w/o)/C_{60}/BCP/Ag) using Paios system in the dark at the range of -1.5–1.5 V with a settling time of 40 ms.

Further focusing on the SCLC region in Figure 3f and S13, the curves were well fitted by Mott-Gurney law:[13–18]

\[
\mu = \frac{8L^3 J}{9\varepsilon \varepsilon_0 V^2}
\]

where \( \mu \) is the charge carrier mobility, \( L \) is the thickness of the perovskite film, \( \varepsilon \) is the relative dielectric constant of perovskite, \( \varepsilon_0 \) is the vacuum permittivity, \( J \) is the dark current, and \( V \) is the applied bias.

Atomic force microscopy (AFM) measurements

The surface topography was inspected by Nanowizard atomic force microscope (JK instrument). The scanning area was 5 \( \mu \)m × 5 \( \mu \)m.
Contact angle measurements

The water contact angle measurement was conducted by OCA 100 (Data Physics Instruments GmbH) in the ambient air at the room temperature. 1 µl sessile drop was applied on the surface for determining the surface contact angle. All the contact angle was measured within 5 seconds after the water droplet was placed in the target surface.

Surface profile and thickness

The thickness of the perovskite films with and w/o interlayers was estimated by Briker Dektakt XT profilometer.

Mott–Schottky (MS) method

MS method was performed on the devices by Paios system in the dark with a constant frequency of 10 kHz and amplitude of 70 mV. The capacitance–voltage ($C^{-2} - V$) characteristics can be obtained from the MS model by the following equation:[16,19]

$$C^{-2} = \frac{2(V_{bi} - V)}{A^2 q \varepsilon \varepsilon_0 N_A}$$

where $C$ is the measured capacitance, $V_{bi}$ is the build-in potential, $V$ is the applied bias, $A$ is the active area, $q$ is the elementary charge, $\varepsilon$ is the relative dielectric constant of perovskite, $\varepsilon_0$ is the vacuum permittivity, and $N_A$ is the charge carrier density.

There are few reports illustrating accurate depletion capacitance as the MS behavior is not readily visible in pristine PSCs based on p-i-n architecture. Thus, the applicability of this analysis is still challenging.[20,21] From the MS plots, $V_{bi}$ can be obtained from the intercept of the linear fitted region with the voltage axis. As illustrated in Figure 4b, the range above 0.5V for the device w/o an interlayer (0.6V for the device with IPH-interlayer) is dominated by charge carrier injection, consequently leading to nonrealistic values of both $V_{bi}$ and $N_A$ by directly employing the equation. In principle, as $V_{bi}$ and $N_A$ are relative values for comparing
the devices with and w/o IPH-interlayer, the obtained or calculated values here are referred to apparent charge carrier density $N$.

*Parallel plate capacitors and electron capture radius*

The capacitance ($C$) based on the devices with the configuration of ITO/IPH or $C_{60}$/Ag, and ITO/interlayer/$C_{60}$ (25 nm)/BCP (3 nm)/Ag were measured by Paios system. The relative dielectric constant ($\varepsilon_r$) of $C_{60}$ or IPH/$C_{60}$ thin films can be calculated by following equation:[4,22]

$$
\varepsilon_r = \frac{Cd}{A\varepsilon_0}
$$

(S7)

where $\varepsilon_0$ is the vacuum permittivity, $A$ is the active area of the parallel plate capacitor (0.105 cm$^2$), and $d$ is the thickness of $C_{60}$ or $C_{60}$/interlayer thin films.

The critical radius ($R_c$) is defined that the charges can escape the electrostatic force with the aid of thermal energy ($kT$), and can be expressed by following:[4,23,24]

$$
R_c = \frac{q^2}{4\pi k T \varepsilon_r \varepsilon_0}
$$

(S8)

where $q$ is electron elementary charge, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_r$ is the relative dielectric constant of $C_{60}$ or $C_{60}$/interlayer thin films.

It is obvious that enhancing $\varepsilon_r$ can reduce $R_c$. As shown in Figure S16, $\varepsilon_r$ could be evaluated by the measurement of parallel plate capacitors based on $C_{60}$ or $C_{60}$/interlayer. Notably, IPH/$C_{60}$ thin film attained a much higher $\varepsilon_r$ than other thin films, revealing considerably reduced $R_c$. Therefore, IPH-interlayer could effectively screen the electrostatic force.[24] This $\varepsilon_r$ difference among the fullerenes could be speculated by the alkyl chain effect (Figure S1) which could influence the polarizability and $\varepsilon_r$.[22,24,25]
2. Figures and Tables

Figure S1. Chemical structures of different fullerenes.
Figure S2. (a) Thickness of NBG perovskite thin film based on ITO glass observed by Dektak profilometer. (b) Estimated thickness of 10 different surface spots of NBG perovskite thin films with and w/o an interlayer.
Figure S3. (a) $J$–$V$ characteristics of the best-performing devices with and w/o an interlayer measured from backward scan under AM 1.5G (1000 W m$^{-2}$) irradiation. The inset shows the corresponding photovoltaic parameters. (b) Stabilized power conversion efficiency (SPCE) under continuous illumination of the best-performing devices. $J$–$V$ characteristics of devices (c) with and w/o IPH interlayer via the forward and backward scans, and (d) the devices with IPH-interlayer measured under different temperature under AM 1.5G (1000 W m$^{-2}$) irradiation.
Figure S4. (a) Transmittance, (b) reflectance, (c) absorptance spectra, and (d) Tauc-plots of the NBG perovskite thin films with and w/o an interlayer.
Figure S5. (a) UPS spectra at the secondary electron region and the valence band maximum region of NBG perovskite. (b) Transmittance, (c) reflectance, (d) absorbance spectra and (e) – (h) Tauc-plots of the different fullerenes on bare ITO/glass substrates.
Figure S6. Band alignments of perovskite/interlayer and perovskite/C_{60} with positive (+), zero (0), and negative (-) conduction band offset (CBO). CBM: conduction band minimum; VBM: valence band maximum; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; $\chi$: the electron affinity. CBO (+): $\chi_{\text{PSK}} > \chi_{\text{IPH}}$; CBO (0): $\chi_{\text{PSK}} = \chi_{\text{PCBM}}$; CBO (-): $\chi_{\text{PSK}} < \chi_{\text{C}_{60}}$. 
Figure S7. Atomic force microscopy (AFM) 2D topography images of (a) NBG pristine perovskite thin film and with interlayer of (b) IPH, (c) PCBM, (d) IPB. Corresponding (a1) to (d1) phase images and (a2) to (d2) 3D views.
Figure S8. Contact angle for a water droplet (1 μL) on NBG perovskite thin films with and w/o an interlayer.
**Figure S9.** High-resolution XPS spectra of Sn 3d for the pristine NBG perovskite with and w/o an interlayer.
Figure S10. Steady-state photoluminescence (PL) pristine NBG perovskite film and with different fullerene derivative/C$_{60}$ thin films based on bare glass substrates.
Figure S11. Dark $J$–$V$ curves of the champion devices with and w/o IPH-interlayer. The semi-logarithmic $J$–$V$ plots can be divided into three regions. Region A presents the leakage current where the device with IPH-interlayer shows one order of magnitude lower value than the device w/o an interlayer. Region B reveals exponential diode comportment, while region C reflects the series resistance ($R_s$) of the whole devices.
Figure S12. (a) The zoomed-in view in high frequency region of Nyquist plots, (b) the equivalent circuit diagram, and (c) Capacitance–frequency plots of NBG PSCs with and w/o an interlayer. \( R_s \): the series resistance; \( R_{\text{rec}} \): the charge recombination resistance; \( C_{\text{rec}} \): charge recombination capacitance.
Figure S13. Dark $J$–$V$ characteristics of electron-only devices (a) w/o, with (b) PCBM, (c) IPB, and (d) IPH interlayer displaying $V_{TFL}$ kink point behavior. (e) Statistics and the average values of the trap density ($n_t$) obtained by space-charge-limited current (SCLC) method.
Figure S14. (a) Nyquist, (b) capacitance–frequency, and (c) light intensity–$V_{OC}$ plots of fresh and aged (stored 1032 h in nitrogen glove box 25 °C) NBG PSCs with and w/o IPH-interlayer. The inset in (a) presents a zoomed-in details of Nyquist plots. (d) PCE tracking plots for champion NBG PSCs (stored in nitrogen glove box at 25 °C) with (5 and 2.5 mg mL$^{-1}$) and w/o IPH-interlayer. (e) Stabilized power conversion efficiency (SPCE) of aged (stored 1032 h in nitrogen glove box 25 °C) NBG PSCs with and w/o IPH-interlayer under continuous illumination for 10 hours.
Figure S15. (a) Photocurrent density ($J_{ph}$) as a function of the effective voltage ($V_{eff}$) for the PSCs with and w/o IPH-interlayer under AM 1.5G (1000 W m$^{-2}$) irradiation. (b) Mott–Schottky plots of the NBG PSCs with and w/o IPH-interlayer. The apparent charge carrier density ($N$) was estimated by Mott-Schottky method.
Figure S16. Capacitance–frequency plots of the devices with the configuration of (a) ITO/IPH or C₆₀/Ag, and (b) ITO/interlayer/C₆₀/BCP (3 nm)/Ag. (c) Schematic of electron capture radius for the interfaces of perovskite/C₆₀ and perovskite/IPH/C₆₀.
Figure S17. (a) J–V characteristics and (b) SPCE of champion single-junction NBG bottom cell ($E_g=1.26$ eV) w/o an interlayer, WBG top cell ($E_g=1.63$ eV) and filtered bottom cell measured from backward scan under AM 1.5G ($1000$ W m$^{-2}$) irradiation.
### Table S1: Summary of NBG PSCs with different interlayers at the interface between perovskite and transport layer.

| Perovskite | Interlayer | $E_g$ (eV) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | PCE (%) | $V_{OC}$ deficit (V) | Ref. |
|------------|------------|-----------|--------------|--------------------------|----|---------|---------------------|------|
| FA$_{0.6}$MA$_{0.4}$Sn$_{0.6}$Pb$_{0.4}$I$_3$ | PFI | 1.22 | 0.78 | 27.22 | 0.74 | 15.85 | 0.44 | [26] |
| FASn$_{0.5}$Pb$_{0.5}$I$_3$ | PCP-Na | - | 0.78 | 28.51 | 0.73 | 16.27 | - | [27] |
| (FASn$_{1.0}$MAPb$_{1.0}$)$_{0.4}$ | PBDB-T: ITIC | 1.25 | 0.86 | 27.92 | 0.75 | 18.03 | 0.39 | [28] |
| Cs$_{0.02}$FA$_{0.475}$MA$_{0.5}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ | EDA | 1.25 | 0.86 | 31.86 | 0.80 | 21.74 | 0.39 | [29] |
| MAPb$_{0.5}$Sn$_{0.5}$I$_3$ | DF-C$_{60}$ | 1.2 | 0.87 | 26.1 | 0.69 | 15.61 | 0.33 | [30] |
| FA$_{0.5}$MA$_{0.5}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ | PCBM | 1.25 | 0.75 | 30.56 | 0.76 | 17.59 | 0.50 | [30] |
| Cs$_{0.02}$ (FA$_{0.83}$MA$_{0.17}$)$_{0.975}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ | IPH | 1.26 | 0.83 | 30.7 | 0.73 | 18.6 | 0.43 | This work |

**Non-fullerene interlayer**

PFI: perfluorinated ionomer; PCP-Na: a pH neutral anionic conjugated polymer with alkylsulfonate side group; PBDB-T: poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b0]dithiophene))-(5,5-(10,30-di-2-thienyl-50,70-bis(2-ethylhexyl)benzo[10,20-c:40,50-c0]dithiophene-4,8-dione)); ITIC: 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:20,30-d0]-s-indaceno[1,2-b:5,6-b0]-dithiophene; EDA: ethylenediamine.

** Fullerene interlayer**

DF-C$_{60}$: hybrid fluoroalkyl-substituted fullerene; PCBM: phenyl-C61-butyric acid methyl ester; IPH: indene-C60-propionic acid hexyl ester.
Table S2 Summary of different parameters of the TRPL spectra based on NBG PSCs with and w/o an interlayer.

| Samples            | $\tau_1$ (ns) | Fraction 1 | $\tau_2$ (ns) | Fraction 2 |
|--------------------|---------------|------------|---------------|------------|
| PSK                | 355           | -          | -             | -          |
| PSK/C60            | 34            | 0.681      | 131           | 0.319      |
| PSK/PCBM/C60       | 33            | 0.649      | 143           | 0.351      |
| PSK/IPB/C60        | 36            | 0.578      | 142           | 0.422      |
| PSK/IPH/C60        | 42            | 0.503      | 170           | 0.497      |

The TRPL data for PSK thin film was fitted with a single-exponential and the rest were fitted with a biexponential functions, revealing a short lifetime ($\tau_1$) and long lifetime ($\tau_2$).
Table S3 Summary of different parameters for NBG PSCs measured in electrical impedance spectroscopy (EIS).

| Devices | $R_s$ (Ω) | $R_{\text{rec}}$ (MΩ) | $C_{\text{rec}}$ (nF) | $\tau_{\text{eis}}$ (ms) |
|---------|-----------|------------------------|------------------------|------------------------|
| IPH     | 16.0      | 28.2                   | 7.2                    | 203                    |
| IPB     | 15.8      | 21.4                   | 7.0                    | 150                    |
| PCBM    | 20.4      | 19.6                   | 6.8                    | 133                    |
| w/o     | 19.6      | 1.9                    | 7.6                    | 14                     |

$R_s$: the series resistance; $R_{\text{rec}}$: the charge recombination resistance; $C_{\text{rec}}$: charge recombination capacitance; $\tau_{\text{eis}}$: charge carrier lifetime; $\tau_{\text{eis}} = R_{\text{rec}}C_{\text{rec}}$. All data were collected by Z-View fitting.
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