Supporting Information

Nanofibrillar conjugated polymer film as an interface layer for highperformance CsPbIBr₂ solar cells with efficiency exceeding 11%

Qian Wang,^{a,b} Yinyan Xu,^{a,b} Lun Zhang,^{a,b} Pujun Niu,^{a,b} Ru Zhou,^c Mei Lyu,^a Guobing Zhang,^{a,b} Hongbo Lu,^{a,b} and Jun Zhu*^{a,b}

^a Special Display and Imaging Technology Innovation Center of Anhui Province, Anhui Province Key Laboratory of Measuring Theory and Precision Instrument, Academy of Opto-Electric Technology, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China.

^b School of Chemistry and Chemical Engineering, Hefei University of Technology,
193 Tunxi Road, Hefei, 230009, China.

^c School of Electrical Engineering and Automation, Hefei University of Technology,
193 Tunxi Road, Hefei, 230009, China.

*Corresponding author (email: jzhu@hfut.edu.cn)

EXPERIMENTAL SECTION

Materials

6,6'-Dibromodi(2-decyltetradecyl)isoindigo (2Br-ID), (3E,7E)-3,7-bis(6-bromo-1-(2decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione (2Br-BIBDF), and 5,5'-bis(trimethylstannyl)-2,2'-dithiophene (2tin-DT) were synthesized according to the reported methods.¹ Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), tri(o-tolyl)phosphine (P(o-tol)₃), and other chemicals were purchased from Sigma-Aldrich Chemical Company, Alfa Aeasar Chemical Company, and Sinopharm Chemical Reagent Co. Ltd., China. Cesium iodide (CsI, 99.9%), lead bromide (PbBr₂, 99.99%), phenyl-C61-butyric acid methyl ester (PC₆₁BM, 99.99%), poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid ester) (PEDOT:PSS, 1.3-1.7 wt % solution in water) were purchased from Xi'an Polymer Light Technology Corp. Dimethyl sulfoxide (DMSO, 99.8%) were purchased from Shanghai Bailingwei Chemical Technology Co., Ltd. Titanium tetrachloride (TiCl₄, Sinopharm Chemical Reagent Co. Ltd., China), 2,2',7,7'-tetra(N,N-bis-p-methoxyaniline)-9,9'-Spiro difluorene (Spiro-OMeTAD, Ningbo Borun), 4-tert-butylpyridine (4-tBP, 96%, Aladdin), bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, 99%, Aladdin), chlorobenzene (99.8%, Sigma-Aldrich). All the chemicals were used without further purification.

Synthesis of conjugated polymer

The conjugated polymer was synthesized according to the the previous reports.¹ Briefly, 2Br-ID (0.1439 g), 2Br-BIBDF (13.6 mg), 2tin-DT (0.07 g), $Pd_2(dba)_3$ (5 mg), $P(o-tol)_3$ (7 mg) and anhydrous chlorobenzene (12 mL) were stirred at 130 °C for 48 h. Then the reaction mixture was added into 80 mL methanol and was stirred for another 2 h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol and dichloromethane. Finally, the remaining black-blue solid was extracted with hot chloroform.

Device fabrication

The FTO substrates were cleaned with acetone, ethanol and deionized water, respectively. After drying, the cleaned FTO substrates were treated with ultravioletozone (UVO) for 30 min, and then a compact TiO₂ (c-TiO₂) electron transport layer was deposited onto the FTO substrate by the chemical bath deposition method.² Prior to preparing the perovskite films, the FTO/c- TiO₂ substrates were re-treated by UVO for 30 min and then quickly transferred to a nitrogen-filled glove box. The CsPbIBr₂ perovskite precursor solution (1.0 M) was prepared by dissolving CsI (260 mg) and PbBr₂ (367 mg) in DMSO (1 mL). The perovskite precursor solution was spincoated at 1000 rpm for 10 s and 2000 rpm for 40 s, then the film was sequentially heated to 30 °C for 5 min, and 250 °C for 5 min. After cooling down to room temperature, the conjugated polymer solution (in chlorobenzene) was spin-coated on the perovskite film at 3000 rpm for 30 s. Subsequently, the Spiro-OMeTAD as hole transport layer (HTL) was deposited by spin-coating at 4000 rpm for 30 s, the precursor solution of Spiro-OMeTAD was prepared by 72.3 mg of Spiro-OMeTAD, 28.8 µL of 4-tBP, and 17.5 µL Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1mL chlorobenzene. Finally, Au was thermally evaporated on the top of Spiro-OMeTAD. The single-hole device and the single-electron device were fabricated with device configurations of FTO/PEDOT:PSS/perovskite/Spiro-OMeTAD/Au and FTO/c-TiO₂/perovskite/PCBM/Au, respectively. The perovskite layers were prepared in the same method as that used for solar cells.

Film and device characterization

The scanning electron microscope (SEM) images were obtained with a field emission scanning electron microscope (Gemini 500). The atomic force microscope (AFM) images were obtained by a Bruker Dimension Icon atomic force microscope. The X-ray diffraction (XRD) patterns were characterized using PANalytical X-Pert PRO MPD (40 kV, 40 mA Cu K α radiation). The J-V curves of solar cells were obtained from a Newport Oriel Sol3A solar simulator under simulated AM 1.5G sunlight at 100 mW cm⁻² irradiances. The light intensity of 100 mW cm⁻² was calibrated by using a standard silicon solar cell. The active area of the device is 0.04 cm². The incident photon-to-electron conversion efficiency (IPCE) measurements were using an IPCE kit (Newport). Ultraviolet-visible (UV-vis) absorption spectra of the perovskite films were obtained by the spectrophotometer (UV2550 UV, Shimadzu). The steady-state PL spectra were measured by a fluorescence spectrophotometer (FluoroMax-4, HORIBA). The time-resolved PL (TRPL) spectra were measured by the Edinburgh FLS1000. X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectra (UPS) were obtained by the Thermo Scientific Escalab 250Xi. The Electrochemical impedance spectra (EIS) measurements were conducted on an electrochemical workstation (CHI660D, Shanghai Chenhua) with the measured frequencies ranged from 100 mHz to 1 MHz at bias voltage of 1.0 V.



Fig. S1 Chemical structure of the conjugated polymer.



Fig. S2 Top-view SEM images and AFM images of CsPbIBr $_2$ /CP films (a) 0.3 mg/mL, (b) 1.0 mg/mL and (c) 3.0 mg/mL.



Fig. S3 XRD patterns of pristine $CsPbIBr_2$ film and the perovskite films deposited with various concentrations of CP.



Fig. S4 The XPS spectra of (a) Cs 3d, (b) I 3d, and (c) Br 3d in the pristine CsPbIBr₂ film, and CsPbIBr₂/CP films.



Fig. S5 Top-view SEM images of CsPbIBr₂/Spiro-OMeTAD film and CsPbIBr₂/0.5 CP /Spiro-OMeTAD film.



Fig. S6 Statistical PCE, V_{OC} , FF and J_{SC} distribution.



Fig. S7 J–V curves of the control and 0.5 CP devices under reverse and forward scan directions.

The state state summary of the photovolu		I IIIIIIIII	FF	PCE	Vaa	
Device		$J_{\rm SC}$	FF (0/)		y ea	Ref.
FTO/c-TiO2/CsPbIBr2/CP/Spiro-	(V)	(mA/cm ²)	(%)	(%)	r Thia	
OMeTAD/Au	1.19	12.09	73.31	11.05	1 1115	WOLK
FTO/TiO ₂ /CsPbIBr ₂ /P3HT: PCBM BHJ/carbon	1.312	11.79	74.47	11.54	2021	[3]
ITO/SnO ₂ /PEIE/CsPbIBr ₂ /Spiro- OMeTAD/MoO ₃ /Ag	1.29	11.00	78.6	11.2	2021	[4]
FTO/TiO ₂ /PEG:CsPbIBr ₂ /Spiro- OMeTAD/Ag	1.21	12.25	74.82	11.10	2020	[5]
FTO/c-TiO ₂ /CsPbIBr ₂ /FA-GO/Carbon	1.318	11.87	70.84	11.08	2021	[6]
ITO/SnO ₂ /MgO/CsPbIBr ₂ /Spiro- OMeTAD/Ag	1.36	11.70	69.35	11.04	2020	[7]
FTO/c-TiO ₂ /CsPbIBr ₂ /Bpy/carbon	1.30	11.77	72.0	11.04	2021	[8]
FTO/c-TiO ₂ /CsPbIBr ₂ /(NiCo) _{1-y} Fe _y O _x / carbon	1.29	12.03	70.58	10.95	2021	[9]
FTO/TiO ₂ /SmBr ₃ /CsPb _{0.95} Sm _{0.05} IBr ₂ /Spiro -OMeTAD/Au	1.17	12.75	73	10.88	2019	[10]
FTO/c-TiO ₂ /CsPbIBr ₂ :ZnBr ₂ / Spiro-OMeTAD/Ag	1.28	11.92	69	10.51	2020	[11]
ITO/TiO2/CsPbIBr2/QS/Carbon	1.298	11.53	69.59	10.41	2021	[12]
FTO/TiO ₂ /Cu ²⁺ -doped CsPbIBr ₂ /Spiro- OMeTAD/Ag	1.21	12.80	67	10.40	2020	[13]
FTO/TiO ₂ /CsBr/CsPbIBr ₂ /CsBr/ Spiro-OMeTAD/Au	1.24	11.76	71	10.33	2021	[14]
FTO/c-TiO ₂ /CsPbIBr ₂ /Sr ²⁺ :CsPbI ₃ QDs/Spiro-OMeTAD/Au	1.20	11.09	77.7	10.32	2021	[15]
ITO/SnO ₂ /CsPbIBr ₂ /YD ₂ -o-C8/ Spiro-OMeTAD/Au	1.37	12.05	61	10.13	2019	[16]
ITO/SnO ₂ /CsXth-doped CsPbIBr ₂ /P3HT/Au	1.30	10.19	73.81	9.78	2019	[17]
FTO/SnO ₂ /TiO ₂ /CsBr/CsPbIBr ₂ /Carbon	1.273	10.91	66	9.31	2019	[18]
FTO/c-TiO ₂ /PMMA/CsPbIBr ₂ /carbon	1.307	11.36	62	9.21	2021	[19]

Table S1. A brief summary of the photovoltaic parameters in high-efficiency CsPbIBr₂ PSCs.

5 m i ig 67.				
Directio n	$V_{\rm OC}$ (V)	$J_{\rm SC}~({ m mA/cm^2})$	FF (%)	PCE(%)
RS	1.183	11.31	66.67	8.92
FS	1.107	10.90	62.82	7.58
RS	1.188	12.69	73.31	11.05
FS	1.143	12.52	71.12	10.18
	Directio n RS FS RS FS	Directio Voc (V) n Voc (V) RS 1.183 FS 1.107 RS 1.188 FS 1.143	Directio V _{OC} (V) J _{SC} (mA/cm ²) n VOC (V) J _{SC} (mA/cm ²) RS 1.183 11.31 FS 1.107 10.90 RS 1.188 12.69 FS 1.143 12.52	Directio V _{OC} (V) J _{SC} (mA/cm ²) FF (%) RS 1.183 11.31 66.67 FS 1.107 10.90 62.82 RS 1.188 12.69 73.31 FS 1.143 12.52 71.12

Table S2. Photovoltaic parameters of the control and 0.5 CP devices under reverse and forward scan directions in **Fig. S7**.

Table S3. EIS parameters analyzed in Fig. 5a with fitting the Nyquist plots.

Sample	$R_{\rm s}\left(\Omega ight)$	$R_{ m tr}$ (Ω)
control	7.55	12698
0.5 CP	11.84	2047

Device Conditions		Aging time	Percentage of the remaining PCE to the initial PCE	Ref.
FTO/c-TiO ₂ /CsPbIBr ₂ /CP/ Spiro-OMeTAD/Au	Air, 25 °C, 20% RH	900 h	91%	This work
ITO/SnO ₂ /PEIE/CsPbIBr ₂ / Spiro-OMeTAD/MoO ₃ /Ag	N ₂ , continuously light- soaking (1 sun)	500 h	80%	[4]
FTO/TiO ₂ /PEG:CsPbIBr ₂ / Spiro-OMeTAD/Ag	Air, 25 °C, 35% RH	600 h	90%	[5]
ITO/SnO ₂ /MgO/CsPbIBr ₂ / Spiro-OMeTAD/Ag	Air, 25 °C, 25% RH	1250 h	90%	[7]
FTO/TiO ₂ /SmBr ₃ /CsPb _{0.95} Sm _{0.05} IBr ₂ /Spiro-OMeTAD/Au	Air; N ₂	24 h; 5 days	70%; 80%	[10]
FTO/c-TiO ₂ /CsPbIBr ₂ :ZnBr ₂ / Spiro-OMeTAD/Ag	Air, 25 °C, 20% RH; N ₂ , 85 °C	30 days; 400 h	91%; 82%	[11]
FTO/TiO ₂ /CsBr/CsPbIBr ₂ /CsBr/ Spiro-OMeTAD/Au	Air, 45% RH	60 h	>60%	[14]
FTO/c-TiO ₂ /CsPbIBr ₂ /Sr ²⁺ :CsPbI ₃ QDs/Spiro-OMeTAD/Au	Air, 25 °C, 20% RH	14 days	90%	[15]
ITO/SnO ₂ /CsPbIBr ₂ /YD ₂ -o-C8/ Spiro-OMeTAD/Au	Air, 25 °C, 30-40% RH	300 h	86%	[16]

Table S4. The long-term stability of high-efficiency CsPbIBr₂ PSCs based on Spiro-OMeTAD as HTL under various conditions

References

- 1 Y. Liu, F. Wang, J. Chen, X. Wang, H. Lu, L. Qiu and G. Zhang, *Macromolecules*, 2018, 51, 370-378.
- 2 Z. Chen, Q. Wang, Y. Xu, R. Zhou, L. Zhang, Y. Huang, L. Hu, M. Lyu and J. Zhu, ACS Appl. Mater. Interfaces, 2021, 13, 24654-24661.
- 3 D. Wang, W. Li, R. Li, W. Sun, J. Wu and Z. Lan, Sol. RRL, 2021, 5, 2100375.
- 4 J. Wang, X. Wu, Y. Liu, Q. Xue, H.-L. Yip, A. K. Y. Jen and Z. Zhu, *Energy Technol.*, 2021, 9, 2100562.
- 5 Y. You, W. Tian, M. Wang, F. Cao, H. Sun and L. Li, *Adv. Mater. Interfaces*, 2020, 7, 2000537.
- 6 J. Du, J. Duan, Q. Guo, Y. Duan, X. Yang, Q. Zhou and Q. Tang, *J. Mater. Chem. A*, 2021, 9, 25418-25425.
- 7 H. Wang, H. Li, S. Cao, M. Wang, J. Chen and Z. Zang, Sol. RRL, 2020, 4, 2000226.
- 8 J. Zhang, J. Duan, Q. Zhang, Q. Guo, F. Yan, X. Yang, Y. Duan and Q. Tang, *Chem. Eng. J.*, 2022, 431, 134230.
- 9 J. Du, J. Duan, X. Yang, Y. Duan, Q. Zhou and Q. Tang, Angew. Chem. Int. Ed., 2021, 60, 10608-1061.
- 10 W. S. Subhani, K. Wang, M. Du, X. Wang and S. Liu, Adv. Energy Mater., 2019, 9, 1803785.
- 11 Y. Long, C. Wang, X. Liu, J. Wang, S. Fu, J. Zhang, Z. Hu and Y. Zhu, *J. Mater. Chem. C*, 2021, 9, 2145-2155.
- 12 D. Wang, W. Li, X. Liu, G. Li, L. Zhang, R. Li, W. Sun, J. Wu and Z. Lan, ACS Appl. Energy Mater., 2021, 4, 5747-5755.
- 13 P. Liu, X. Yang, Y. Chen, H. Xiang, W. Wang, R. Ran, W. Zhou and Z. Shao, ACS Appl. Mater. Interfaces, 2020, 12, 23984-23994.
- 14 X. Jiang, W. S. Subhani, K. Wang, H. Wang, L. Duan, M. Du, S. Pang and S. Liu, *Adv. Mater. Interfaces*, 2021, 8, 2001994.
- 15 Y. Xu, Q. Wang, L. Zhang, M. Lyu, H. Lu, T. Bai, F. Liu, M. Wang and J. Zhu, *Solar RRL*, 2021, 5, 2100669.
- 16 S. Yang, Z. Guo, L. Gao, F. Yu, C. Zhang, M. Fan, G. Wei and T. Ma, Sol. RRL, 2019, 3, 1900212.
- 17 Z. Wang, A. K. Baranwal, M. A. kamarudin, C. H. Ng, M. Pandey, T. Ma and S. Hayase, *Nano Energy*, 2019, 59, 258-267.
- 18 W. Zhu, W. Chai, Z. Zhang, D. Chen, J. Chang, S. F. Liu, J. Zhang, C. Zhang and Y. Hao, Org. Electron., 2019, 74, 103-109.
- 19 W. Chai, J. Ma, W. Zhu, D. Chen, H. Xi, J. Zhang, C. Zhang and Y. Hao, ACS Appl. Mater. Interfaces, 2021, 13, 2868-2878.