

1 **Supplementary Information**

2 **From 20% Single-Junction Organic Photovoltaic to 26% Perovskite/Organic**

3 **Tandem Solar Cells: Self-Assembled Hole Transport Molecules Matter**

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## 1 **1. Device fabrication**

### 2 **OSCs device fabrication**

3 The OSC devices were fabricated with the conventional configuration of  
4 glass/ITO/SAMs/active layer/C60/BCP/Ag. The patterned ITO-coated glass substrate  
5 ( $15 \Omega/\text{sq}$ ) was cleaned with detergent and deionized water ultrasonic cleaning 20 min,  
6 then continuously cleaned three times with acetone, and isopropanol for 15 min of  
7 each step. After that the substrate was dried with a nitrogen gun and then placed in an  
8 ultraviolet-ozone cleaning machine for 20 min. This step can further remove the  
9 organic residue on the substrate surface and improve the hydrophilicity of the  
10 substrate surface. The 4PADCBCB or 4PADCBCB+TCB (weight ratio of 1:1) were  
11 dissolved in isopropanol (IPA) with a concentration of 0.5 mg/mL and placed into an  
12 ultrasonic bath for 20 min. The SAM solution (65  $\mu\text{L}$  for a  $1.5 \times 1.5 \text{ cm}^2$  substrate)  
13 was applied directly onto the ITO substrate for 40 s followed by a spin-coating step at  
14 3000 rpm for 30 s. The ITO/SAM substrate was then placed onto a hotplate and  
15 annealed at  $100^\circ\text{C}$  for 10 min. Finally, the ITO/SAM substrates were transferred  
16 inside a dry nitrogen glove box for solar cell fabrication. The PM6, BTP-eC9, Y6 and  
17 PC<sub>71</sub>BM were purchased from organotec.ltd. For the PM6: BTP-eC9 system, the  
18 PM6:BTP-eC9 solution was prepared by dissolving blends with a weight ratio of  
19 1:1.2 in chloroform (total concentration 15.4 mg/mL) and stirred at room temperature  
20 for 2 hours. The active layer was spin-coated on the ITO/SAM substrates at 3500 rpm  
21 and then annealed 5 min at  $80^\circ\text{C}$ . Finally, C60 (10 nm)/BCP (5 nm)/Ag (100 nm)

1 layers were deposited to complete the device fabrication.

## 2 **Wide-bandgap perovskite single-junction device fabrication**

3 The substrates were then spin-coated with NiO<sub>x</sub> (10 mg/mL in deionized water)  
4 nanoparticle dispersion. Then, the films were transferred to a nitrogen-filled glovebox  
5 and the Me-4PACz (1 mg/mL in IPA) was spin-coated on the substrates at 4,000 rpm  
6 for 30 s and heated at 100°C for 10 min. The 1 M perovskite  
7 (Cs<sub>0.25</sub>FA<sub>0.75</sub>Pb(Br<sub>0.5</sub>I<sub>0.5</sub>)<sub>3</sub>) precursor solution used contains 129 mg FAI, 65 mg CsI,  
8 275 mg PbBr<sub>2</sub>, and 115 mg PbI<sub>2</sub>, which were dissolved in 1 mL mixed solvent of  
9 DMF:DMSO (v/v = 4:1). Then, the precursor solution was shaken overnight at 60°C.  
10 For the spin-coating process, the substrate was spun at 4,000 rpm for 45 s with an  
11 acceleration of 4,000 rpm/s, and 200 mL of MeAc was slowly dropped at 15 s before  
12 the spin-coating ended. The perovskite  
13 films were then annealed at 100°C for 15 min. Then, the C60 (10 nm)/BCP (5 nm)/Ag  
14 (100 nm) layers were deposited to complete the device fabrication.

## 15 **Perovskite-organic tandem device fabrication**

16 After completing the deposition of the BCP layer, Ag (1 nm)/MoO<sub>x</sub> (15 nm) was  
17 thermally evaporated on top of BCP and the film was brought back to the nitrogen-  
18 filled glovebox, then completed the deposition of the SAM layer. For the narrow  
19 band-gap PM6:BTP-eC9 system, the solution was prepared by dissolving blends with  
20 a weight ratio of 1:1:0.2 in chloroform (total concentration 15.4 mg/mL) and stirred at  
21 room temperature for 2 hours. The active layer was spin-coated on the ITO/SAM

1 substrates at 3500 rpm and then annealed 5 min at 80 °C. Finally, C60 (10 nm)/BCP  
2 (5 nm)/Ag (100 nm) layers were deposited to complete the device fabrication.

### 3 **2. Device performance characterization**

4 The  $J$ - $V$  characteristics were performed in N<sub>2</sub>-filled glovebox under AM 1.5G (100  
5 mW/cm<sup>2</sup>) by using a Keithley 2400 source meter unit and an AAA solar simulator  
6 (SS-F5-3A, Enli Technology CO., Ltd.) calibrated by a standard Si photovoltaic cell.  
7 The external quantum efficiency (EQE) was measured by a certified incident photon  
8 to electron conversion (IPCE) equipment (QE-R) from Enli Technology Co., Lt. The  
9 light intensity at each wavelength was calibrated using a standard monocrystalline Si  
10 photovoltaic cell. The bias illumination obtained by applying a 500 nm short-pass  
11 filter, and an 800 nm long-pass filter was used for the measurements of the bottom  
12 subcell and the front subcell of perovskite-OPV TSC, respectively.

### 13 **The analysis of $J_{ph}$ vs $V_{eff}$ relationships**

14 The definition of  $J_{ph}$  is the current density under illumination ( $J_L$ ) minus the dark  
15 current density ( $J_D$ ), and  $V_0$  refers to the voltage value when  $J_{ph} = 0$ . Accordingly,  $V_{eff}$   
16  $= V_0 - V_{appl}$ , where  $V_{appl}$  represents applied voltage, has a clear meaning. Importantly,  
17 when  $V_{eff}$  reaches a high value ( $> 2V$ ) it is normally believed that generated excitons  
18 are fully collected, in which  $J_{ph}$  is equal to saturated current density ( $J_{sat}$ ). Then, we  
19 can calculate  $J_{SC}/J_{sat}$  and  $J_{max}/J_{sat}$  to describe exciton dissociation ( $\eta_{diss}$ ) and charge  
20 collection ( $\eta_{coll}$ ) efficiency.  $J_{max}$  is the  $J_{ph}$  at the maximal output point.

### 21 **Transient photovoltage (TPV) and transient photocurrent (TPC)**

1 For TPV, the measurement was conducted under 1 sun conditions by illuminating the  
2 device with a white light-emitting diode, and the champion device is set to the open-  
3 circuit condition. For TPC, the champion device is set to the short-circuit condition in  
4 dark. The output signal was collected by key sight oscilloscope.

## 5 **Electrochemical analysis**

6 Mott-Schottky characteristics and Nyquist plots were conducted using a PARSTAT  
7 4000A electrochemical workstation, employing a three-electrode setup. For the curve  
8 fitting of Mott-Schottky plots, the data were extracted by linear fitting the drop region  
9 of Mott-Schottky plots, and  $V_{bi}$  was obtained via the intercept of the straight line with  
10 the X axis.

## 11 **Hole Mobility Measurements**

12 The mobilities were measured by using a space charge limited current (SCLC) model  
13 with the hole-only device of glass/ITO/SAMs/PM6: BTP-eC9/MoO3/Ag. Hole  
14 mobility was obtained by fitting the current density-voltage curves and calculated by  
15 the equation<sup>1</sup>:

16 
$$J(V) = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^2} \quad \#(1)$$

17 Where  $J$  is current density,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-14}$  F/cm),  $\epsilon_r$  is  
18 the relative permittivity of the material (assumed to 3),  $\mu$  is hole mobility or electron  
19 mobility,  $V$  is applied voltage and  $L$  is the thickness of film ( $\sim 110$  nm).

## 20 **EQE<sub>EL</sub> measurements**

21 EQEEL measurements were done using a home-built setup using a Keithley 2400 to

1 inject current to the solar cells. Emission photon-flux from the solar cells was  
 2 recorded using a Si detector (Hamamatsu s1337-1010BQ) and a Keithley 6482  
 3 picoammeter.

#### 4 **Urbach energy ( $E_U$ )**

5  $E_U$  can be calculated from the slope of the straight line by plotting  $\ln(\alpha)$  against the  
 6 incident photon energy (E), which follows the straight-line equation below:

$$7 \quad \ln \alpha(E) = \ln \alpha_0 + \frac{E}{E_u} - \frac{E_g}{E_u} \quad \#(2)$$

### 8 **3. Characterization of SAM**

#### 9 **Instruments and characterization**

##### 10 **Nuclear magnetic resonance (NMR) spectroscopy**

11  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on Bruker (AVANCE III 400MHz).

12 X-ray photoelectron spectroscopy (XPS) was measured by Thermo Scientific K-  
 13 Alpha.

##### 14 **Contact angle measurements**

15 The contact angles of water and formamide (FA) on SAMs coated ITO were  
 16 measured by a video optical contact angle meter (DSA-100 (KRUSSE Germany)).

17 Then the surface free energy was calculated by Owens-Wendt method:<sup>2, 3</sup>

$$18 \quad \gamma_L \times (1 + \cos\theta) = 2 \times \left( \gamma_L^d \cdot \gamma_{sv}^d \right)^{\frac{1}{2}} + 2 \times \left( \gamma_L^p \cdot \gamma_{sv}^p \right)^{\frac{1}{2}} \quad \#(3)$$

19 where  $\gamma_L$  and  $\gamma_{sv}$  are surface free energy of the probe liquid and sample, respectively.

20 The  $\theta$  is the contact  $\gamma_L$  angle of the sample. The Flory-Huggins interaction parameter

1  $\chi_{\text{donor-acceptor}}$  for blends to show the binary miscibility was calculated from the  
2 equation:

3 
$$\chi_{\text{donor-acceptor}} = K \left( \gamma_{\text{donor}}^{\frac{1}{2}} - \gamma_{\text{acceptor}}^{\frac{1}{2}} \right)^2 \quad (4)$$

4 where  $\gamma$  is the surface energy of the material,  $K$  is the proportionality constant.

## 5 **GIWAXS and XRD Measurement**

6 GIWAXS measurements were performed at the Synchrotron & Printable Electronic  
7 Lab, Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic University  
8 with SAXSFocus 3.0 (GKINST Co., LTD.) equipped with a Cu X-ray Source (8.05  
9 keV, 1.54 Å) and an EIGER 2R 500K detector. The incident angle during the  
10 measurement was maintained at 0.5° and the distance between sample and detector  
11 was 132 mm.

12 For the GIWAXS and XRD measurement of SAM layers, the films were prepared by  
13 spin-coating the control and TCB-treated SAM precursor solutions (2 mg/mL in IPA)  
14 at 500 rpm for 30 s, followed by annealing at 130 °C for 5 min, the thicker films are  
15 beneficial to obtain better signals.

## 16 **Theoretical calculations**

17 All the calculations of the model compounds studied in this work were performed  
18 using the Gaussian 09 software package. Ground state geometry optimizations of  
19 4PADCB, and TCB are calculated by DFT at the B3LYP/6-31G (d, p) (empirical  
20 dispersion = gd3bj) level. The visualization of the molecular orbitals and ESP  
21 distribution was performed using GaussView 6.0.16 and VMD software.<sup>4</sup> The



1 reduced density gradient analysis was performed using MultiWfn3.8 software.<sup>5, 6</sup>

## 2 **4. Characterization of the active layer**

### 3 **Film-depth-dependent light absorption and composition distribution**

4 Film-depth-dependent light absorption was carried out with an in-situ spectrometer

5 (PU100, Shaanxi Puguang Weishi Co. Ltd.) equipped with a soft plasma-ion source.

6 A 100 W power with an input pressure of ~10 Pa (oxygen) was used to generate soft

7 ionic source. The surface of the target film is gradually etched by the soft ion source,

8 without damage to the materials underneath. The absorption for the film during

9 etching was in-situ monitored by a spectrometer.

### 10 **Atomic Force Microscopy (AFM) measurements**

11 Topographic images of the films were obtained from a Bruker atomic force

12 microscopy (AFM) with the type of dimension edge with Scan Asyst in the tapping

13 mode using an etched silicon cantilever at a nominal load of ~2 nN, the scanning rate

14 for a 1  $\mu\text{m} \times 1 \mu\text{m}$  image size was 0.9 Hz and 5  $\mu\text{m} \times 5 \mu\text{m}$  image size was 1.0 Hz.

### 15 **HAADF-TEM measurements**

16 The films were floated off the substrates in deionized water and collected on lacey

17 carbon coated TEM grids (Electron Microscopy Sciences). HAADF-TEM were

18 performed on a Thermo Fischer Talos-200S TEM equipped with an electron

19 monochromator and a Gatan Imaging Filter (GIF) Quantum 966.

### 20 **GIWAXS and GISAXS Measurement**

21 The samples were fabricated by spin-coating the active layer precursor solutions onto

1 Si substrates. The incidence angles are  $0.12^\circ$  and the distances between sample and  
 2 detector are 132 mm (GIWAXS) and 1000 mm (GISAXS) respectively. One  
 3 dimensional experimental data were obtained with the SGTools software package  
 4 programmed by Zhao et al.<sup>7</sup>

## 5 Data analysis.

6 The ordering degree of SAMs was quantified by using the Herman's orientation factor  
 7 ( $f$ ), which is defined as follows:

$$8 \quad f = \frac{1}{2}(3\langle \cos^2\theta \rangle - 1) \quad \#(5)$$

9 where the  $\langle \cos^2\theta \rangle$  is the average value of the square of the cosine of the azimuthal  
 10 angle for the scattering peak, which is calculated as follows:

$$11 \quad \langle \cos^2\theta \rangle = \frac{\int_{\min}^{\pi/2} I(\theta) \cos^2(\theta) \sin(\theta) d\theta}{\int_{\min}^{\pi/2} I(\theta) \sin(\theta) d\theta} \quad \#(6)$$

12 where  $I(\theta)$  is the intensity at an azimuthal angle of  $\theta$ .

13 The structural information of blend films such as the period of arrangement and  
 14 lamellar stacking spacing is obtained via the Bragg equation, as well as the crystal  
 15 coherence length (CCL) can be obtained from the Scherrer formula,<sup>8</sup> and the specific  
 16 expressions of the Bragg equation and Scherrer formula are as follows:

$$17 \quad d = \frac{\lambda}{2\sin(\theta)} = \frac{2\pi}{q} \quad \#(7)$$

$$18 \quad CCL = \frac{K\lambda}{FWHM \cdot \cos(\theta)} \quad \#(8)$$

1 where  $d$  is the lamellar stacking spacing, and  $CCL$  is the crystal domain along the  
 2 specified direction called crystal coherence length, which is generally considered to  
 3 be equivalent to the grain size.  $\lambda$  is the value of X-ray wavelength;  $K$  is a  
 4 dimensionless shape factor,<sup>9</sup> generally taken as  $K = 0.89$ ; FWHM is the half-peak  
 5 width of the scattering peak;  $\theta$  is the scattering angle.

## 6 GISAXS fitting model

7 To quantify and compare the phase separation, the IP (in plane) scattering profiles are  
 8 fitted with a model that describes the scattering contribution of each phase, the fitting  
 9 equation is shown in Eq. (1):

$$10 \quad I(q) = \frac{A_1}{[1 + (q\xi)^2]^2} + A_2 \langle P(q,R) \rangle S(q,R,\eta,D) + B \quad (9)$$

11 where the first term was the so-called Debye-Anderson-Brumberger (DAB) term<sup>10</sup>,  
 12 modeling the scattering from the amorphous intermixing domains, and  $\xi$  is the  
 13 average correlation length of the amorphous domain.

14 The second term is the scattering intensity contribution from the small molecule  
 15 pure domains in the co-monomer, where  $P(q, R)$  is the shape factor of the pure  
 16 domains.  $S(q, R, \eta, D)$  is the structure factor of pure domains, and the fractal-like  
 17 network model is generally used to describe the cluster domains in the films  
 18 expressed as follows:

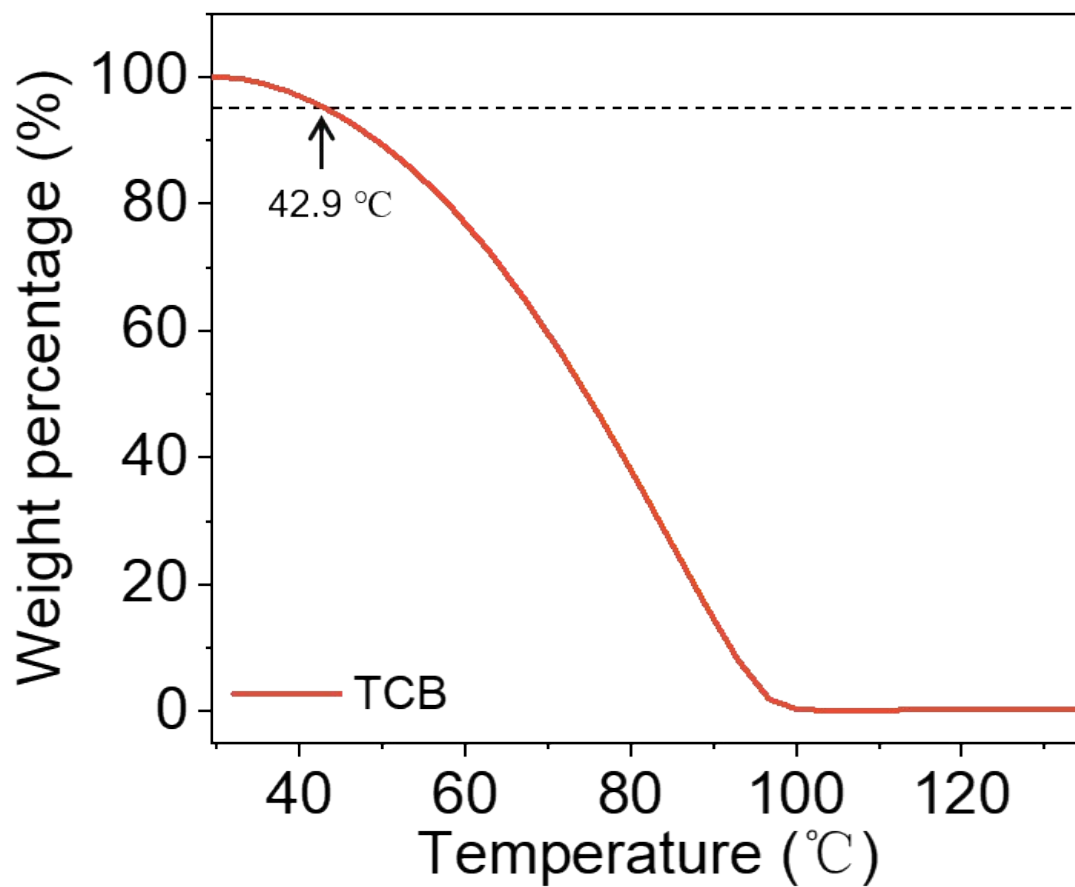
$$19 \quad S(q) = 1 + \frac{\sin[(D-1)\tan^{-1}(q\eta)]}{(qR)^D} \cdot \frac{D\Gamma(D-1)}{\left[1 + \frac{1}{(q\eta)^2}\right]^{\frac{(D-1)}{2}}} \quad (10)$$

20 where  $R$  is the mean radius,  $\eta$  is the coherence length of the fractal network, and  $D$  is  
 21 the fractal dimension of the structure. The average domain size can be estimated by

1 the Guinier radius of the fractal-like network  $R_g$  expressed as follows:

2 
$$R_g = \left[ \frac{D(D+1)}{2} \right]^{\frac{1}{2}} \eta^{\#(11)}$$

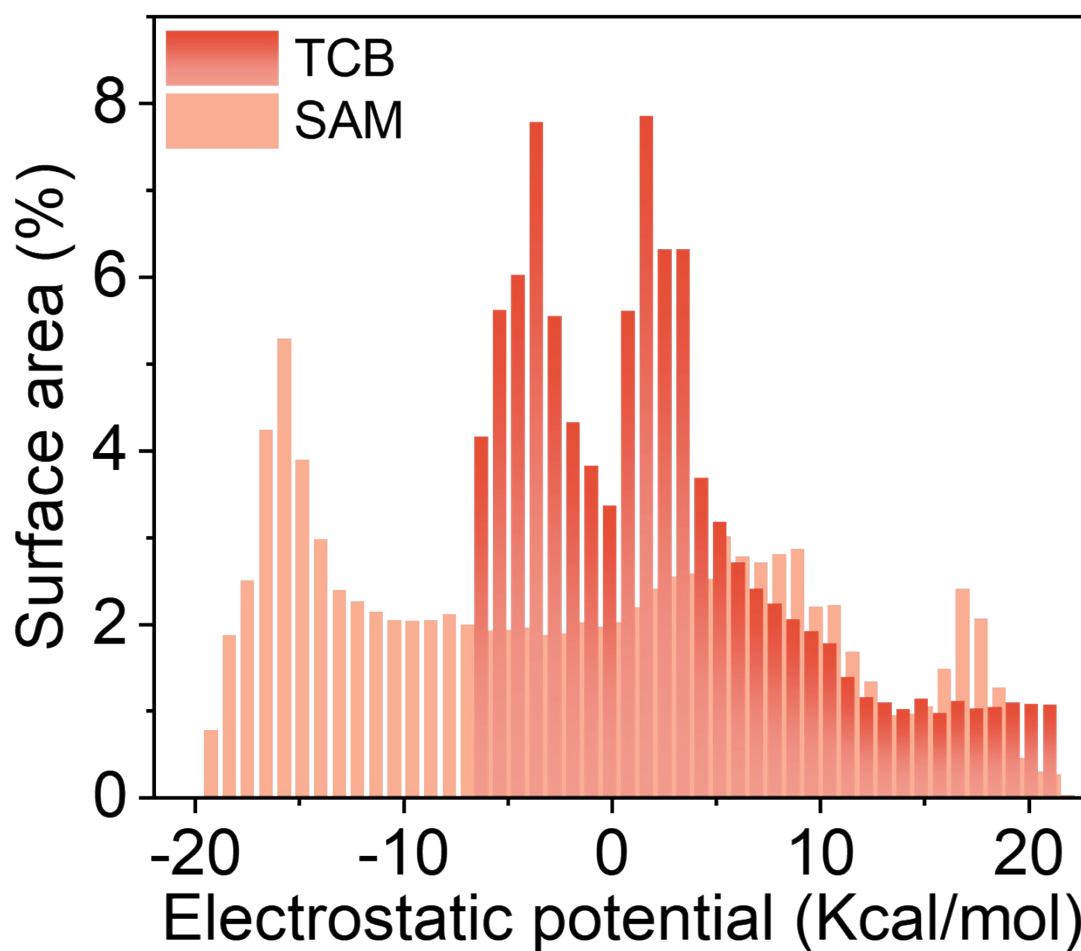
3



4

5 **Fig. S1** TGA plots of TCB at a scan rate of  $10^{\circ}\text{C min}^{-1}$  under inert atmosphere.

6



1

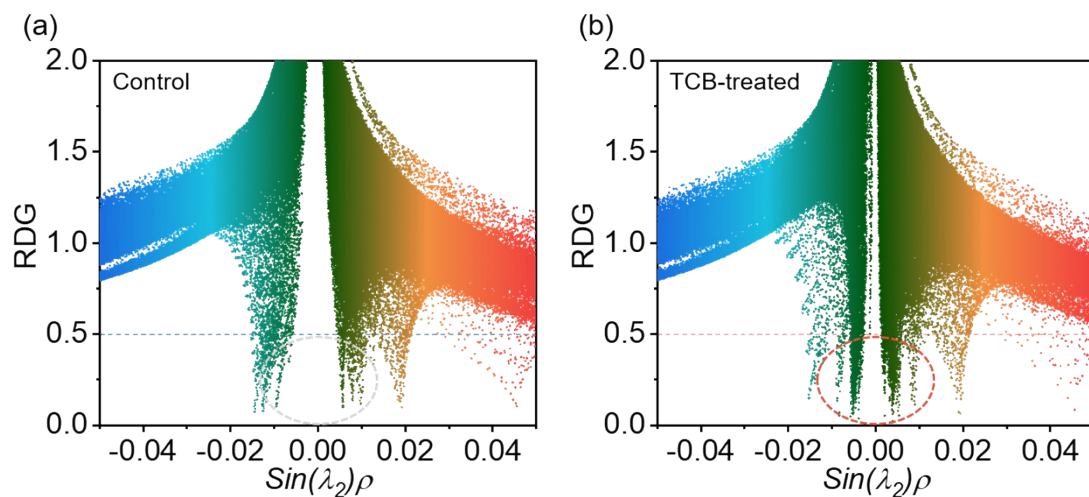
2 **Fig. S2** Quantitative analysis of the histograms of electrostatic potential area

3 distribution of TCB and SAM.

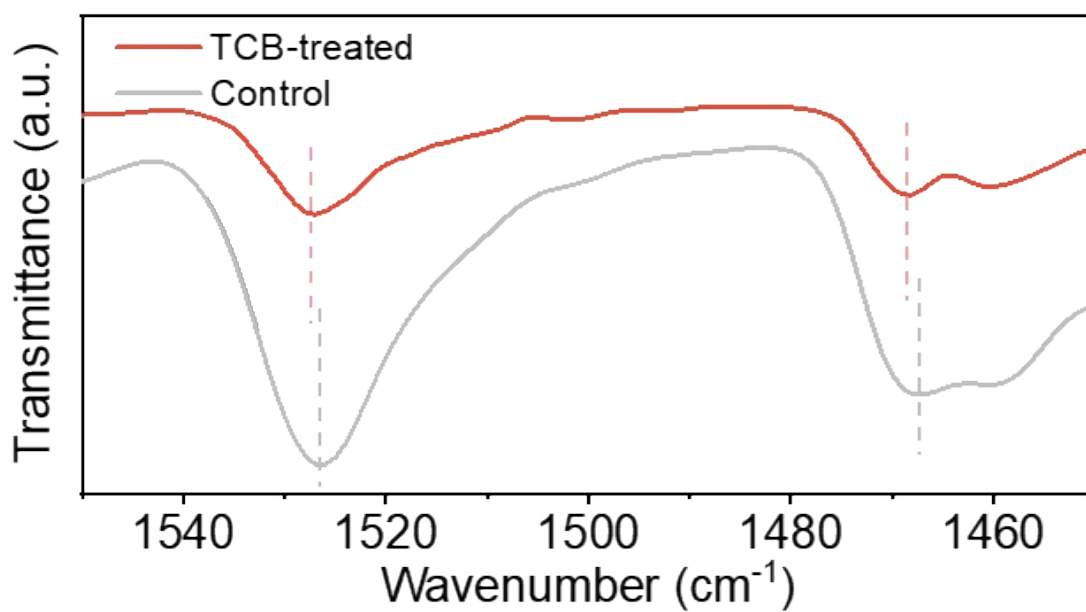
4

5 **Table S1** The the overall average ESP values of DCB core and TCB, respectively.

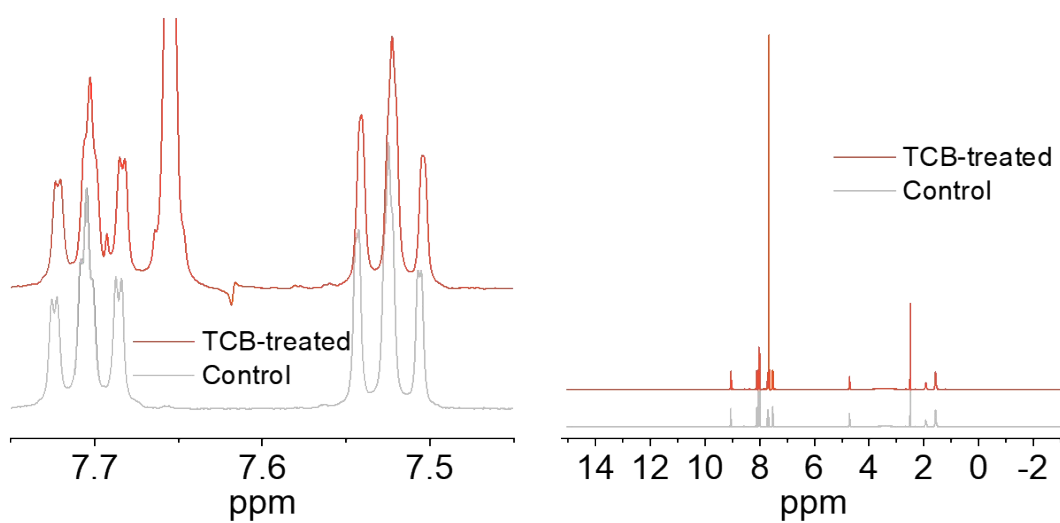
	Overall average value (kcal/mol)
DCB Core	-1.11
TCB	2.33



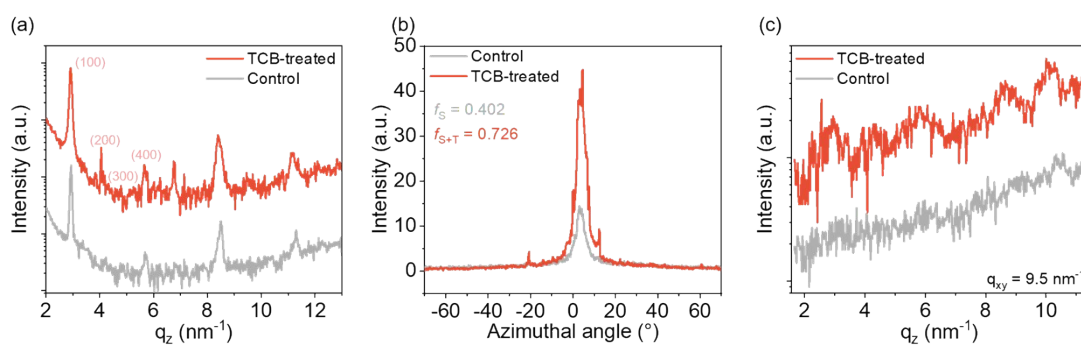
**Fig. S3** The functions of RDG and Sign ( $\lambda_2$ ) $\rho$  for (a) control and (b) TCB-treated SAM.



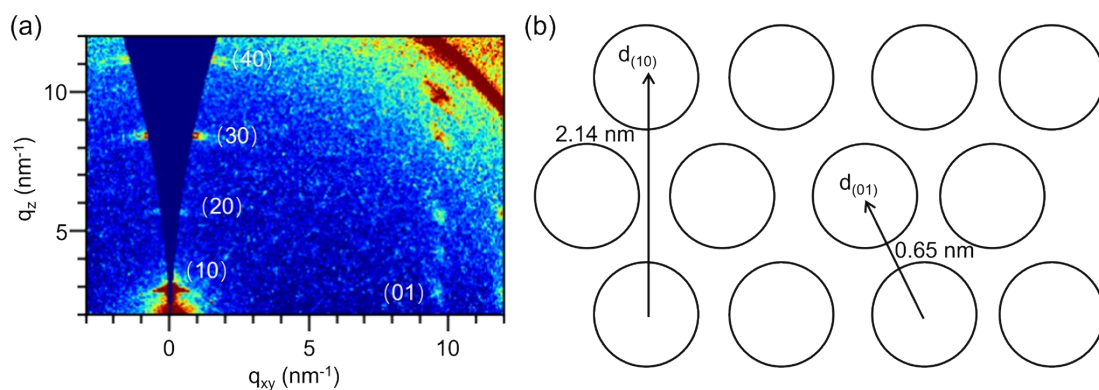
**Fig. S4** The FTIR spectra of control and TCB-treated SAM.



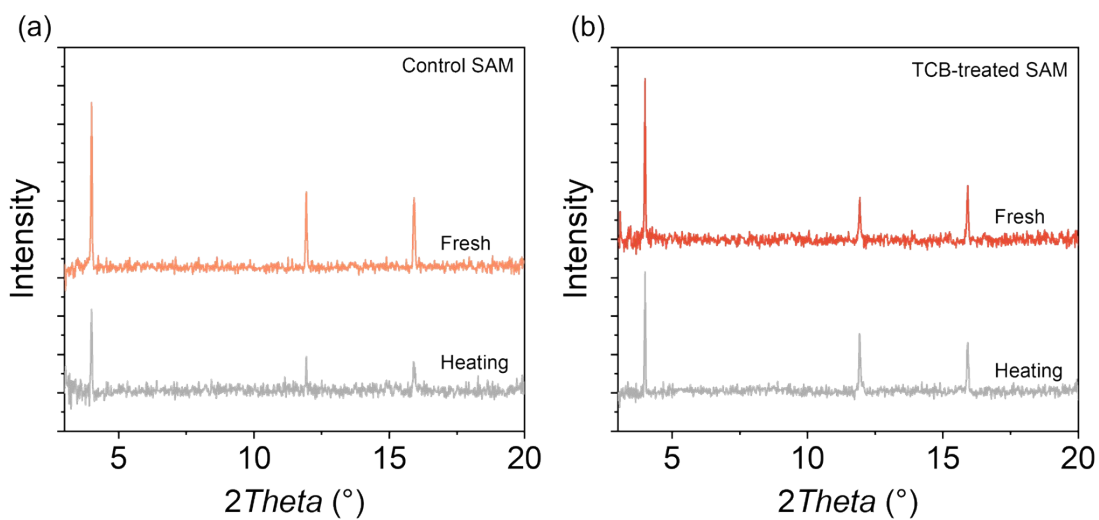
**Fig. S5**  $^1\text{H}$  NMR spectra of control and TCB-treated SAM.



**Fig. S6** The scattering profile of SAMs on (a) OOP direction, (b) azimuth degree and (c)  $q_{xy} \approx 9.5 \text{ nm}^{-1}$ .

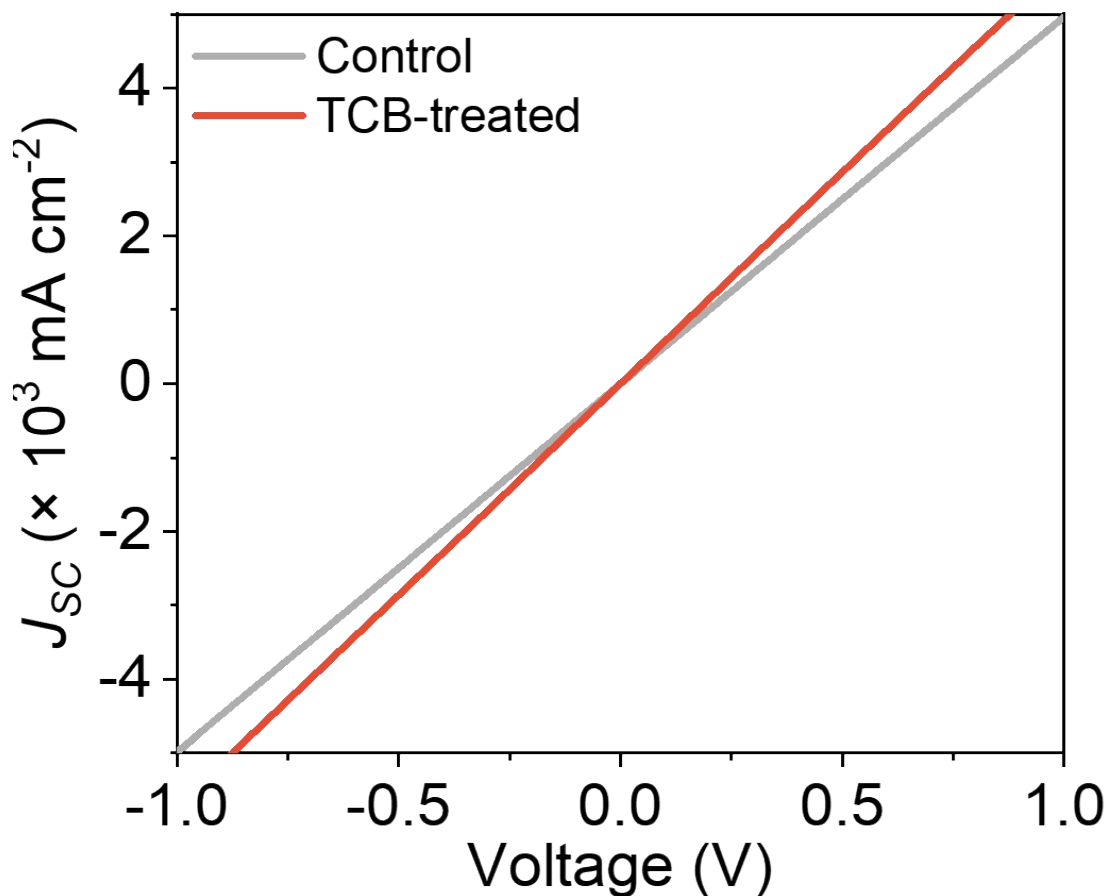


**Fig. S7** (a) 2D GIWAXS patterns of TCB-treated SAM layer. (b) Representation of the 2D hex and rectangular unit.



**Fig. S8** (a)(b) XRD patterns of control and TCB-treated SAM layer before and after ageing tests of thermal annealing





1

2 **Fig. S9** (a)  $J$ - $V$  dark curves of the device with the structure of ITO/control and TCB-  
3 treated SAM/Ag.

4

5 **Table S2** Detailed device parameters with varied concentration of TCB.

TCB Concentration (mg/mL)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
0.1	0.860	28.38	79.63	19.44
0.3	0.862	28.57	79.41	19.54
0.5	0.863	28.83	80.64	20.06
0.8	0.863	28.57	79.74	19.67
1.0	0.863	28.45	79.69	19.57

1 Table S3 Detailed device parameters with varied TA temperatures of SAM layer.

Temperature (°C)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
80	0.863	28.64	78.94	19.52
100	0.863	28.83	80.64	20.06
120	0.864	28.79	78.85	19.62

2



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计量器具名称  
Description

非富勒烯有机太阳能电池  
Non-fullerene organic solar cells

型号/规格  
Model/Type

非富勒烯有机太阳能电池  
Non-fullerene organic solar cells

制造厂  
Manufacturer

深圳职业技术大学霍夫曼先进材料研究院  
Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic University

出厂编号  
Serial No.

SX-6

设备管理编号  
Equipment No.

接收日期  
Receipt on

2024 年 12 月 25 日  
Y M D

结论  
Conclusion

见校准结果  
Shown in the results of calibration

校准日期  
Calibration on

2024 年 12 月 25 日  
Y M D

发布日期  
Issue on

2025 年 01 月 03 日  
Y M D

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Authorized by

吴江宏 吴江宏

核 验  
Reviewed by

易国贤 易国贤

校 准  
Calibrated by

梅书刚 梅书刚



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Temperature

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Reference documents for the calibration:

JF1622-2017 太阳能电池校准规范: 光电性能 C.S. for Solar Cells: Photoelectric Properties

5. 本次校准所使用的主要计量标准器具:

Major standards of measurement used in the calibration:

设备名称/型号规格/测量范围	编号	证书号/有效期/溯源单位	计量特性
Name of Equipment	Serial No.	Certificate No./Due Date	Metrological
Model/Type/Range		/Traceability to	Characteristic
ABET 稳态太阳模拟器	374	NY202400537	光谱匹配度: A级
1000W full spectrum solar		/2025-12-03	辐照度不均匀性: A级
simulator		/本中心	辐照度不稳定性: A级
/SIN3000/(300~1300)W/m²			
标准太阳能电池	13/01/2014	GXg2024-06295	$L_{rel}=2.2\%$ , $k=2$
Standard Solar Cell		/2025-09-24	
/RR_257_0/ 1sc; (1~200)m A		/中国计量院	
标准源表	4051271	DBB202403401	电压: $U_{rel}=0.1\%$ , 电
Standard Source Meter		/2025-02-26	流: $I_{rel}=0.1\%$ ( $k=2$ )
/2420/(0~60)V, (0~3)A		/本中心	DCV: $U_{rel}=0.1\%$ , DCA: $I_{rel}=0.1\%$ ( $k=2$ )

— 本说明页以下空白 —

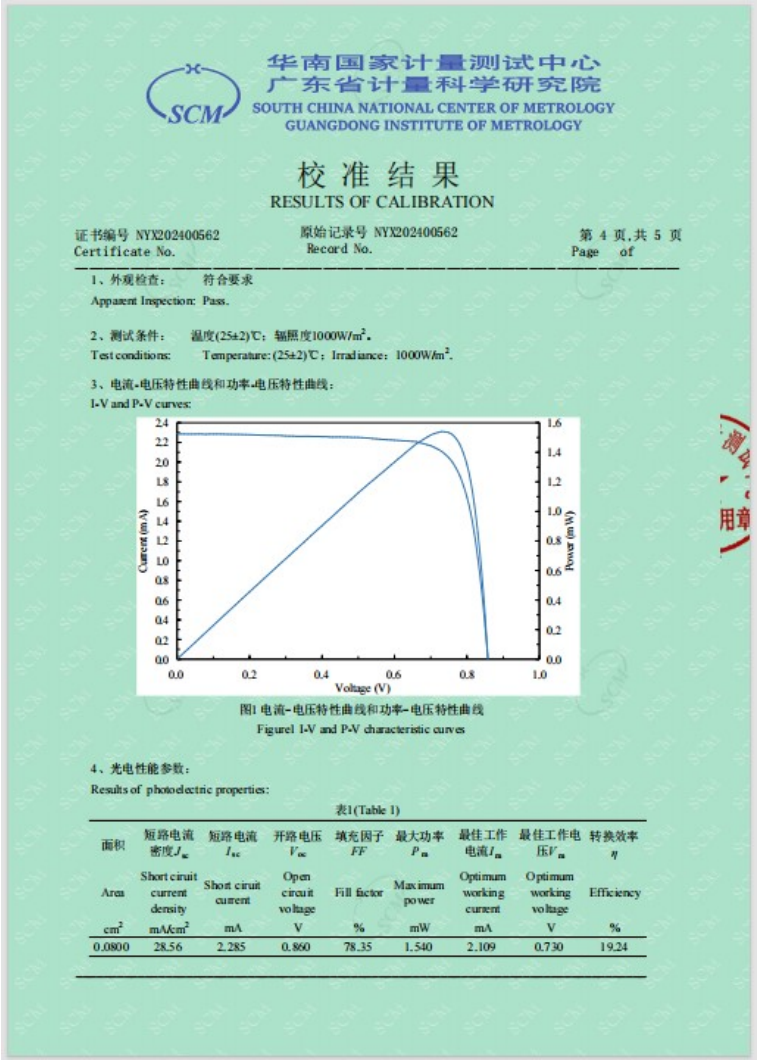
注: 1. 本证书校准结果只与受校准仪器有关。The results relate only to the items calibrated.

Note: 2. 未经本机构书面批准, 不得部分复制此证书。This certificate shall not be reproduced except in full, without the written approval of our laboratory.

3. “客户名称”、“联络信息”由委托方提供, “制造厂”、“型号规格”、“出厂编号”以及“设备编号”为仪器上标注。委托方对上面内容如有异议, 须在收到证书后二十个工作日内提出。

The information Name of the Customer and Contact Information are provided by client, and the Manufacturer, Model/Type, Serial No. and Equipment No. are marked on the item. Client shall submit any objection within 20 working days after receiving the certificate for the information above.

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2 **Fig. S10** Certified Efficiency of PM6:BTP-eC9 binary OSCs device based on TCB-

3 treated SAM.

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1 **Table S4** Summary of the photovoltaic parameter of the device based on control and

2 TCB-treated SAM.

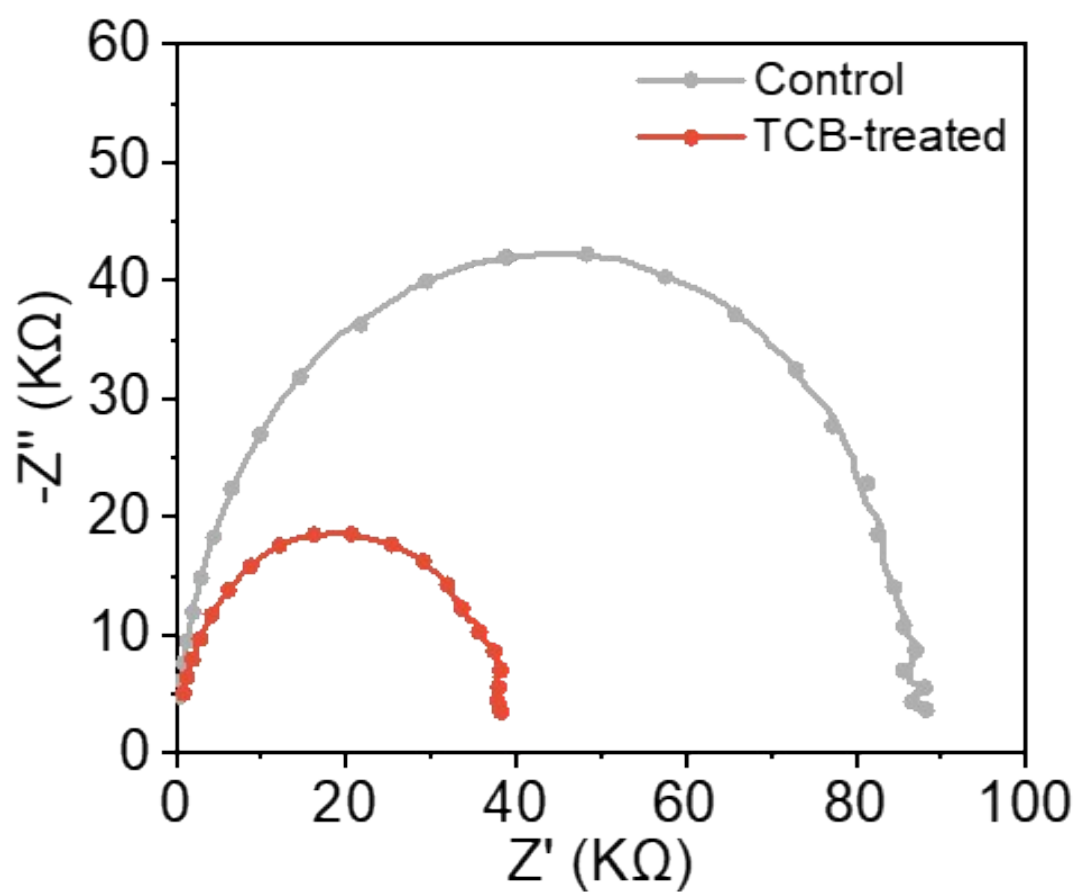
Active layers	Conditions	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE(Average) (%)
PM6:BTP-eC9	Control	0.859	28.43	79.25	19.35
	Target	0.863	28.83	80.64	20.06
PM6:L8-BO	Control	0.909	25.88	78.72	18.51
	Target	0.910	26.68	78.91	19.16
PM6:Y6	Control	0.835	27.19	75.67	17.18
	Target	0.845	27.67	76.40	17.83
PM6:Y6:PC <sub>71</sub> BM	Control	0.843	27.21	76.79	17.62
	Target	0.853	27.22	77.72	18.04

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2 **Fig. S11** Nyquist plots of devices based on control and TCB-treated SAM layer.

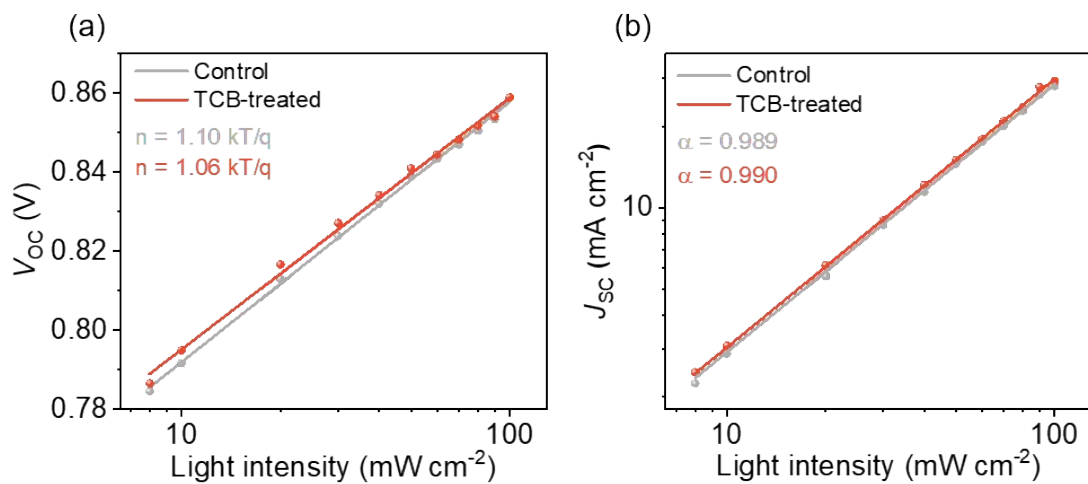
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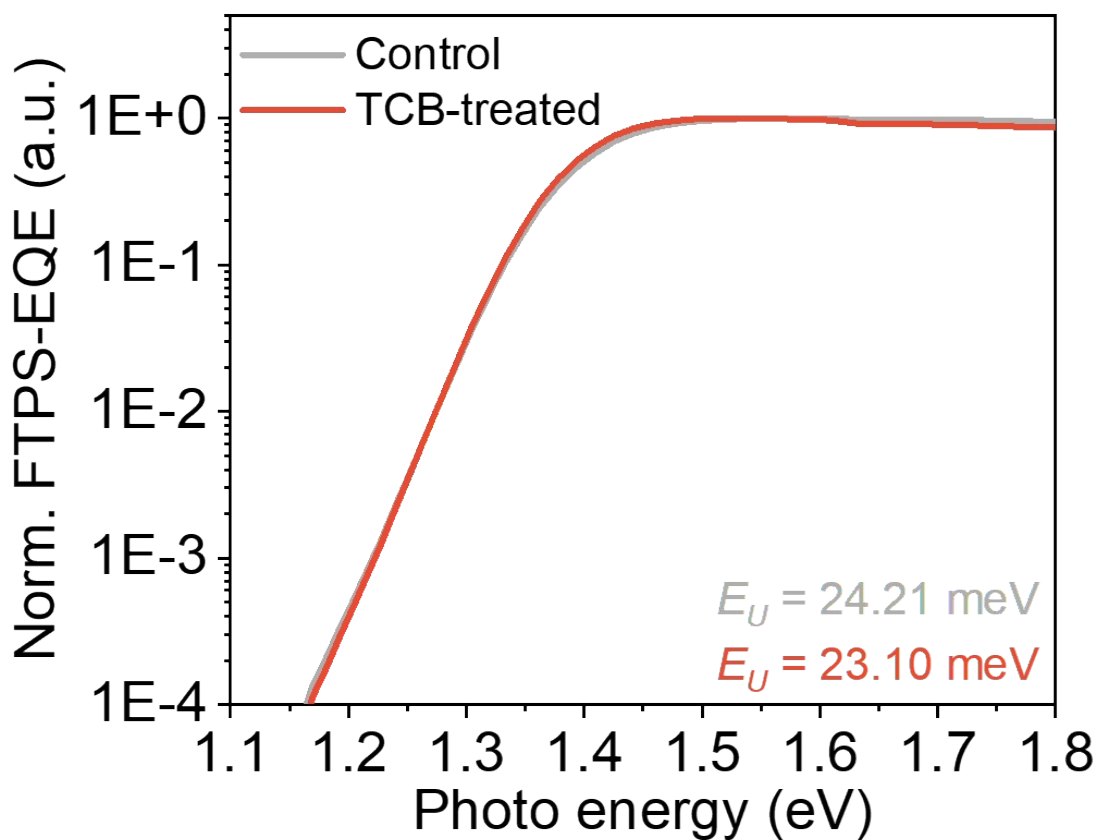
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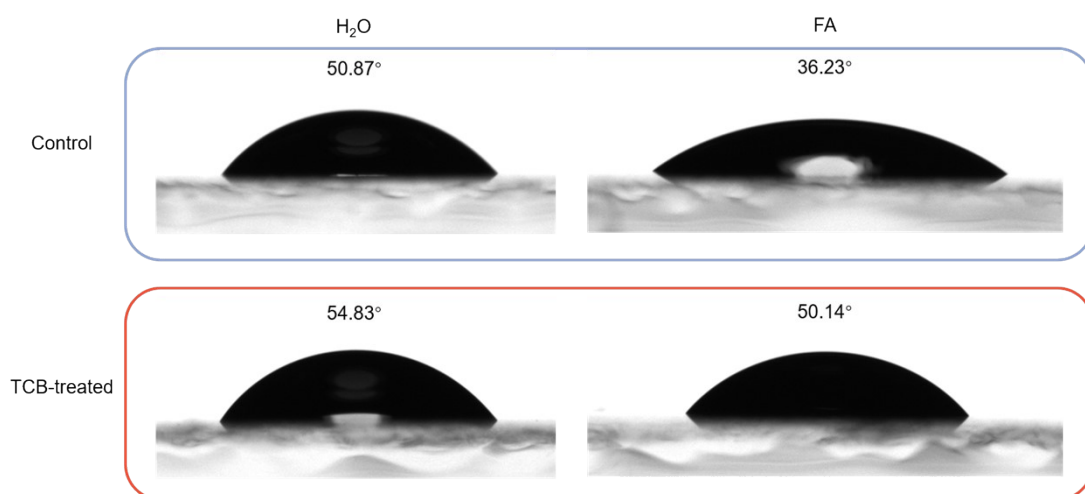


**Fig. S12**  $V_{oc}$  and  $J_{sc}$  with different light intensity.



**Fig. S13** FTPS-EQEs of the device based on control and TCB-treated SAM layer.

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3 **Fig. S14** Photographs of water and formamide droplets in contact with control and  
 4 TCB-treated SAM layer.

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9 **Table S5** Surface energy ( $\gamma_s$ ) of control and TCB-treated SAM layers.

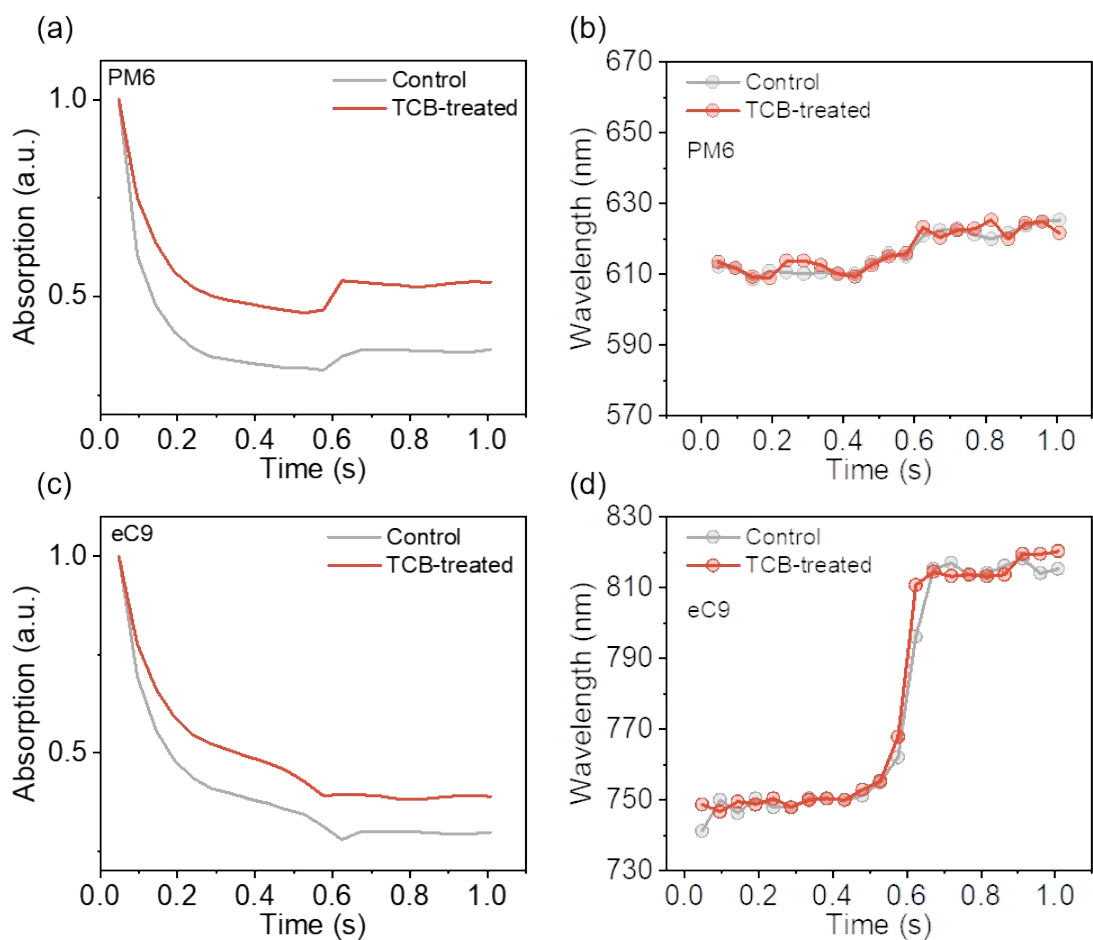
HTL	Contact angle (°)		$\gamma_s$ (mN m <sup>-1</sup> )
	H <sub>2</sub> O	FA	
SAM	50.87	36.23	49.47
SAM+TCB	54.83	50.14	45.12

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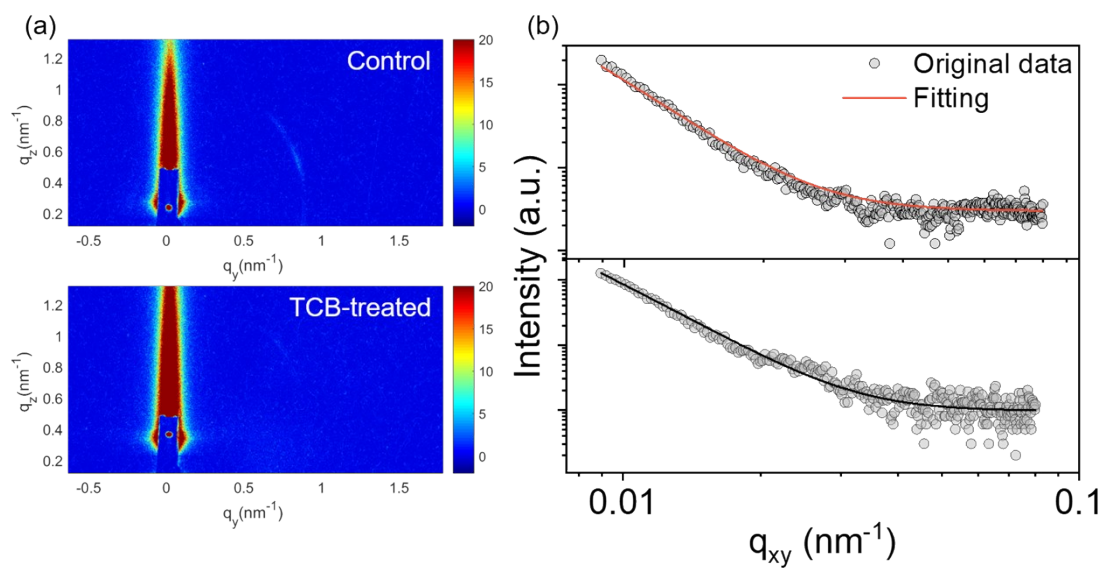
2 **Fig. S15** The time evolutions of absorption peak of blend films during spin-coating.

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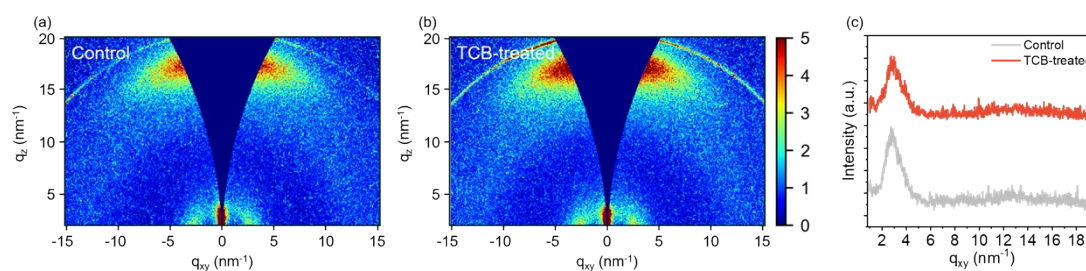
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**Fig. S16** (a) GISAXS patterns and (b) scattering profiles of Yoneda peaks.

**Table S6** Fitting data obtained from GISAXS patterns.

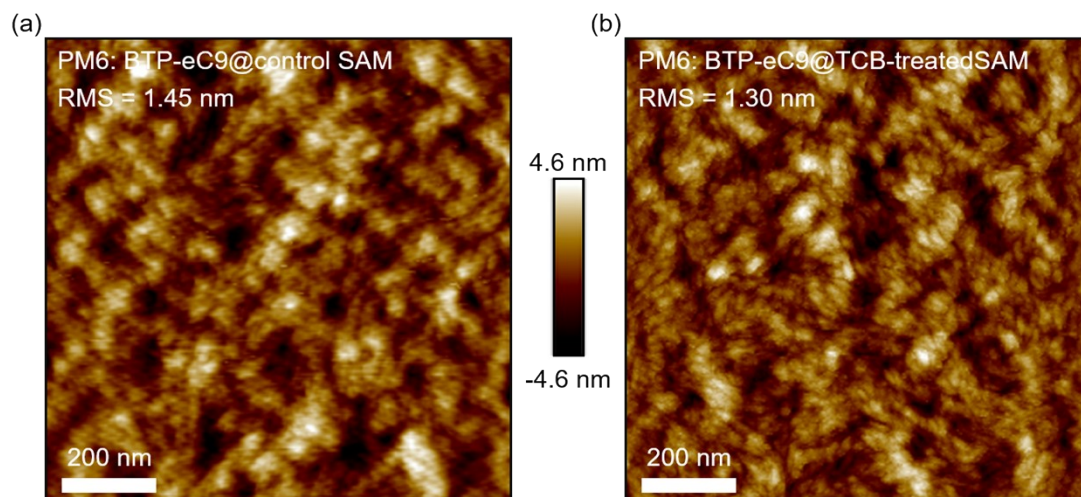
Conditions	$\xi$ (nm)	D	$\eta$ (nm)	$Rg$ (nm)
Control	30.3	1.9	9.4	15.6
TCB-treated	29.0	2.1	9.5	17.8



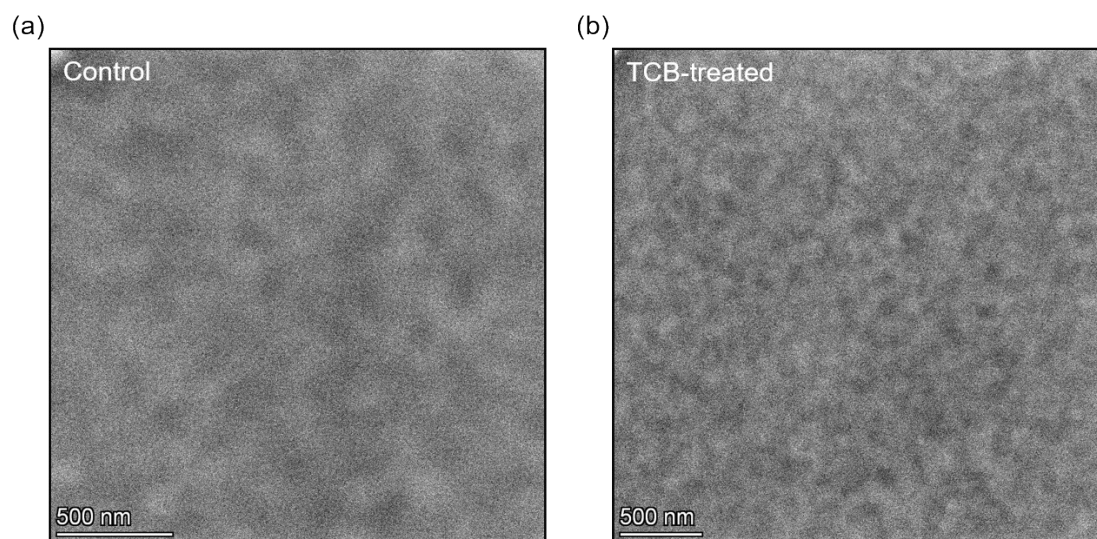
**Fig. S17** GIWAXS patterns and scattering profiles of active layer based on (a) control and (b) TCB-treated SAM layer.

**Table S7** Detailed (010) peak information in the OOP direction of active layer based on control and TCB-treated SAM layer.

Conditions	peak position (nm <sup>-1</sup> )	FWHM (nm <sup>-1</sup> )	<i>d</i> -spacing (nm)	<i>CCL</i> (nm)
Control	17.38	2.057	0.362	5.47
TCB-treated	17.45	2.001	0.360	5.62

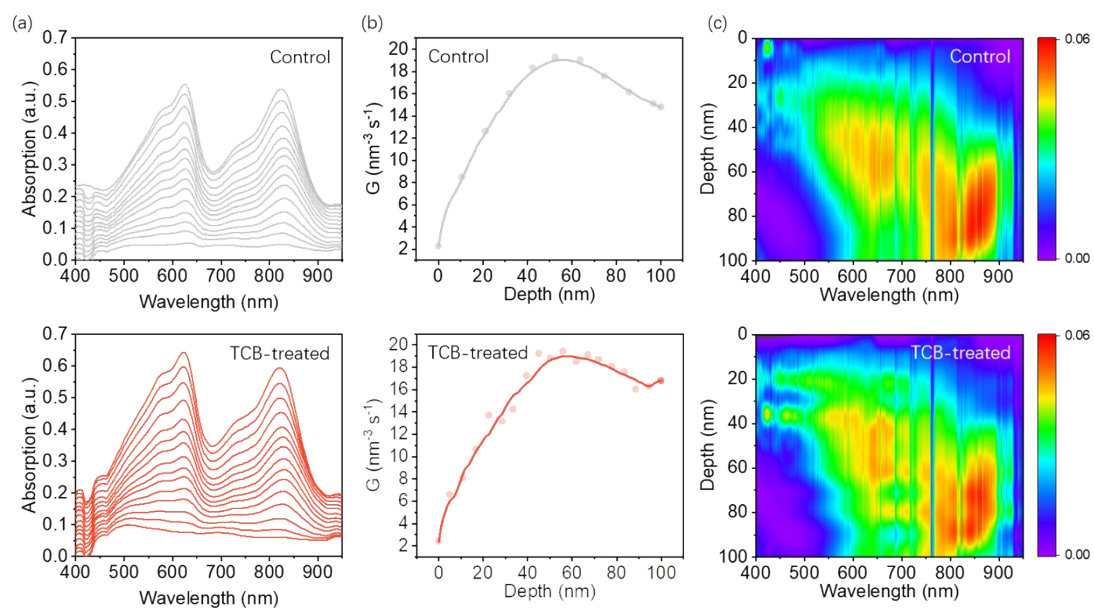


**Fig. S18** AFM height images of active layer on (a) control and (b) TCB-treated SAM layer.



**Fig. S19** TEM images of active layer on (a) control and (b) TCB-treated SAM layer.

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3 **Fig. S20** (a) Film-depth-dependent absorption spectra, (b) exciton generation rate and

4 c) contours of active layer on control and TCB-treated SAM layers.

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2 **Table S8.** The photovoltaic parameters of single junction and tandem devices.

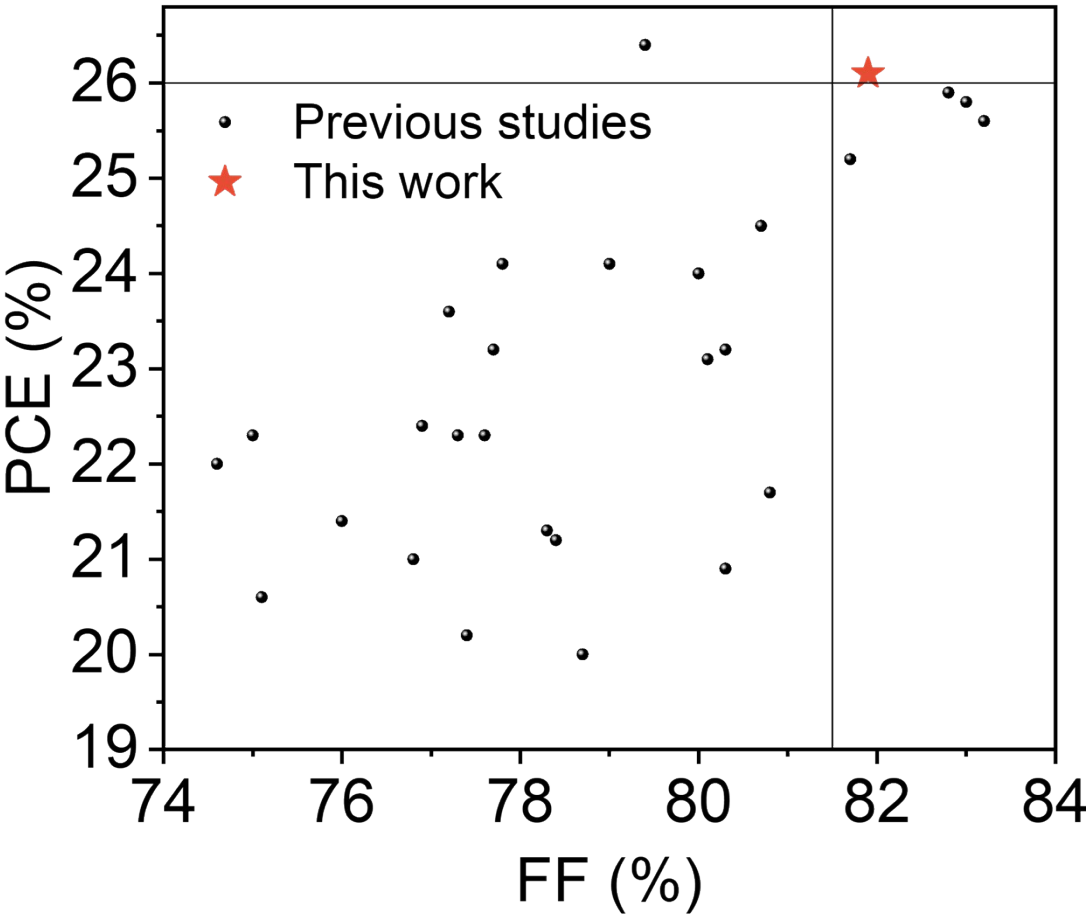
Band gap	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1.85eV PSCs	1.300	15.97	82.98	17.24
1.36eV OSCs	0.858	28.90	79.68	19.75
Tandem	2.131	14.95	81.90	26.09

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8 **Fig. S21** Statistical PCE versus FF of perovskite/organic solar cells in this work and

1 results reported in the literature.

2 **Table S9** Summary of photovoltaic performance of perovskite/organic solar cells in

3 the literature.

$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	Ref.
1.96	13.3	80.3	20.9	11
2.05	13.4	76.8	21.0	12
1.88	15.7	74.6	22.0	13
2.06	14.8	77.2	23.6 (22.9 certified)	14
1.96	13.8	78.4	21.2	15
2.15	14.0	80.0	24.0 (23.1 certified)	16
2.10	13.1	75.1	20.6	17
1.94	13.1	78.7	20.0	18
2.22	12.7	76.0	21.4	19
2.07	13.9	77.3	22.3	20
2.15	13.4	80.3	23.2	21
2.07	13.9	76.9	22.4 (21.4 certified)	22
2.06	13.3	78.3	21.3	23
2.10	14.2	77.7	23.2	24
2.07	13.0	80.8	21.7	25
2.14	14.2	80.7	24.5	26
2.10	13.6	77.6	22.3	27
2.20	14.2	77.8	24.1	28
2.12	14.1	75.0	22.3	29
2.09	14.6	79.0	24.1	30

2.06	12.7	77.4	20.2	31
2.11	13.7	80.1	23.1	32
2.15	14.4	81.7	25.2 (24.3 certified)	33
2.12	14.7	83.0	25.8 (25.0 certified)	34
2.16	15.4	79.4	26.4 (25.7 certified)	35
2.13	14.6	82.8	25.9	36
2.12	14.3	83.2	25.6 (24.7 certified)	37
2.13	14.9	81.9	26.09	This work

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