

## Supporting Information

Jiejie Wan,<sup>a</sup> Zijian Zhang,<sup>a</sup> Jinping Lin,<sup>a</sup> Zejiang Li,<sup>d</sup> Haifen Liu,<sup>b</sup> Qiaohong Li,<sup>c</sup> Shaopeng Yang<sup>a,b</sup> and Lixin Wang<sup>\*a,b,c</sup>

<sup>a</sup>Hebei Key Laboratory of Photo-Electricity Information and Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China

<sup>b</sup>National-Local Joint Engineering Laboratory of New Energy Photoelectric Devices, College of Physics Science and Technology, Hebei University, Baoding 071002, China

<sup>c</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.

<sup>d</sup>College of Chemistry and Materials Science, Hebei University, Baoding 071002, China,

\*Corresponding author: E-mail: [wanglx2015@hbu.edu.cn](mailto:wanglx2015@hbu.edu.cn)

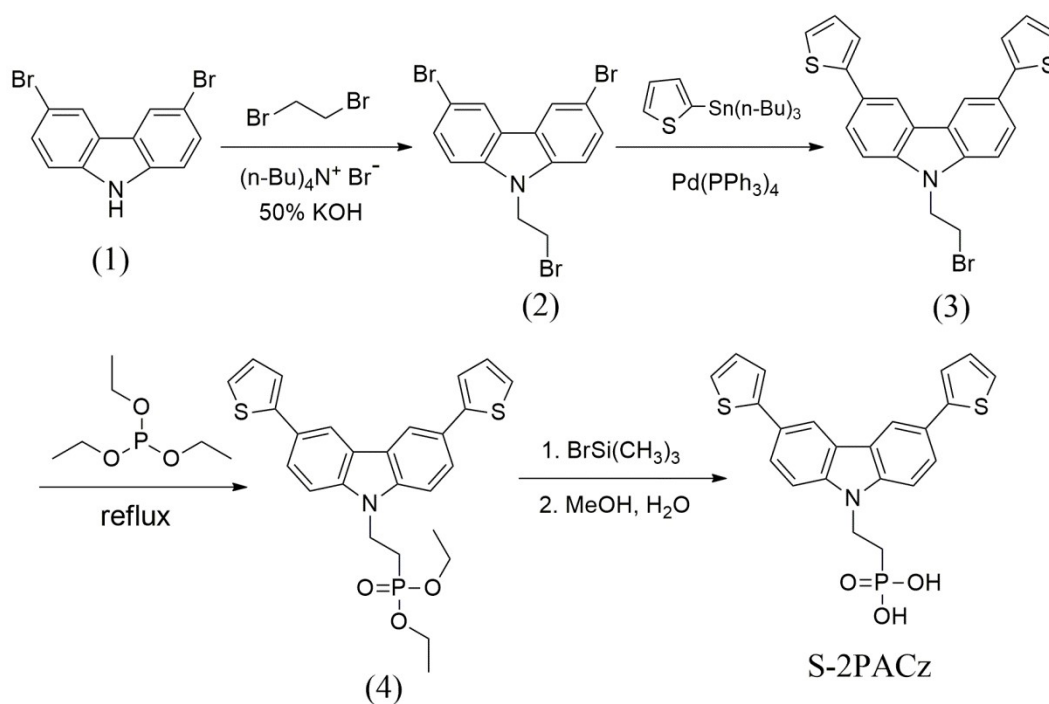
### Characterizations and measurements

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AVANCEIII 600 MHz spectrometer. The chemical shift ( $\delta$ ) values are given in ppm and are referenced to residual solvent peaks. The DFT calculations were implemented in Gaussian 16. The ground-state equilibrium geometries of structures were fully optimized with density functional theory (DFT) using B3LYP functional and 6-31G(d,p) basis sets, with D3 dispersion correction of Grimme<sup>1-2</sup>. During photovoltaic *J-V* curve measurements, a non-reflective mask with an aperture of 0.08 cm<sup>2</sup> was used. The light-intensity-dependent  $V_{OC}$  measurement was measured under a solar simulator (SS-X50, ENLITECH, Taiwan) with variable light intensity. The external quantum efficiency (EQE) spectra were measured by quantum efficiency measurement system (QTEsT HIFINITY 5, CROWNTECH, USA) in air. The absorption spectra were measured on a Hitachi U-3900/3900H UV-vis spectrophotometer. The surface morphological characterizations of the perovskite films were performed by using SEM (NovaNanoSEM450, USA) at a 10 kV accelerating voltage. The roughness of the films was evaluated via AFM (Bruker, Multi-Mode 8). The steady-state PL were measured under excitation of a 470 nm pulsed laser with a power density of 15  $\mu$ J/cm<sup>2</sup>, based on an FLS920 (Edinburgh Instruments) fluorescence spectrometer. The PL mapping and TRPL were performed by confocal fluorescence microscopy (ISS fastFLIM) with 405

nm, 1 MHz in ambient air. A Micro Capture Pro coupled with ImageJ software was applied to obtain the water contact angles of the substrates. XRD were measured using X-ray diffractometer (D8 ADVANCE, Bruker AXS, Germany) with Cu K $\alpha$  radiation source in ambient air. XPS and UPS measurements were performed using a surface analysis system (ThermoFisher, ESCALAB 250Xi) equipped with a He discharge lamp ( $h\nu = 21.22$  eV) and a monochromatic Al-K $\alpha$  x-ray gun. The X-ray spot size was 500  $\mu\text{m}$  in diameter.

## Synthesis of the SAM materials

### 1. Synthesis of S-2PACz



**Scheme 1.** Synthetic route to S-2PACz

### 3, 6-dibromo-9-(2-bromoethyl)-9H-carbazole (2):

3, 6-dibromo-9H-carbazole (2 g, 6.15 mmol) was dissolved in 1, 2-dibromoethane (40 mL), followed by tetrabutylammonium bromide (0.198 g, 0.61 mmol) and 50% KOH aqueous solution (53 mL). The reactant was stirred at 80 °C for 1 day. Upon completion, the crude product is extracted with ethyl acetate. The organic layer is dried with anhydrous Mg<sub>2</sub>SO<sub>4</sub> and the solvent is removed under reduced pressure. Purification was carried out by column chromatography using ethyl acetate:petroleum ether (1:20 in volume ) as the eluent to obtain

2.1 g of white crystalline substance (75% yield)  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (s, 2H), 7.57 (d,  $J = 6.0$  Hz, 2H), 7.29 (d,  $J = 6.0$  Hz, 2H), 4.65 (m, 2H), 3.65 (t,  $J = 7.2$  Hz, 2H).

**9-(2-bromoethyl)-3,6-di(thiophen-2-yl)-9H-carbazole (3):**

Compound **2** (1 g, 2.32 mmol) and 2-(tributyltin) thiophene (2.5 *eq.*) were dissolved in anhydrous toluene (20 mL), and were stirred under nitrogen for 20 minutes. Then,  $\text{Pd}(\text{PPh}_3)_4$  (0.076 g, 0.066 mmol) was added, and the mixture was heated to 100 °C and maintained with stirring for 24 hours. The mixture was poured into 100 mL water and extracted with ethyl acetate. The organic phase was dried by anhydrous  $\text{Mg}_2\text{SO}_4$ , concentrated, and purified by column chromatography to yield 0.87 g of the target product as a white solid (85% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (s, 2H), 7.75 (dd,  $J = 8.4, 1.8$  Hz, 2H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.36 (m, 2H), 7.28 (d,  $J = 5.4$  Hz, 2H), 7.12 (m, 2H), 4.69 (t,  $J = 7.2$  Hz, 2H), 3.69 (t,  $J = 7.2$  Hz, 2H).

**diethyl (2-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)ethyl)phosphonate (4):**

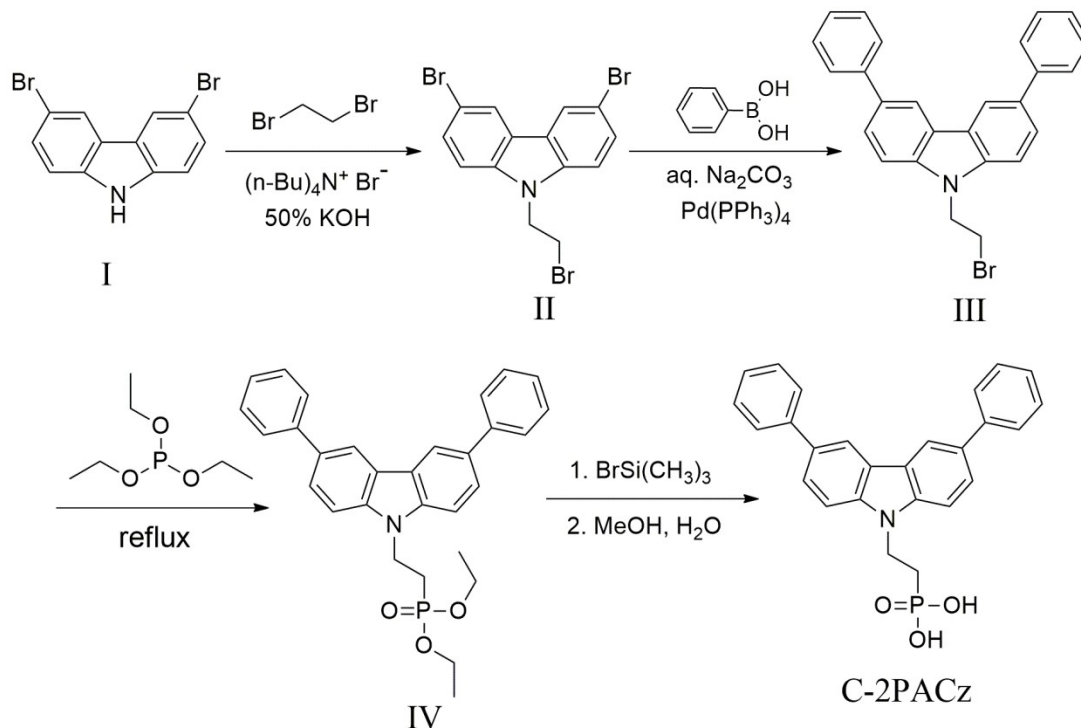
Compound **3** (1 g, 2.28 mmol) was dissolved in 15 mL of triethylphosphite and the reaction mixture was heated at reflux for 24 h. After the reaction is complete, the solvent is distilled off under reduced pressure. The crude product was purified by column chromatography (acetone:petroleum ether, 1:4, v/v) to obtain a transparent liquid (1.02 g, 88% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (s, 2H), 7.76 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.43 (d,  $J = 8.4$  Hz, 2H), 7.37 (d,  $J = 2.4$  Hz, 2H), 7.28 (m, 2H), 7.12 (dd,  $J = 5.2, 3.5$  Hz, 2H), 4.62 (m, 2H), 4.07 (m, 4H), 2.31 (m, 2H), 1.28 (t,  $J = 7.2$  Hz, 6H).

**(2-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl)ethyl)phosphonic acid (S-2PACz):**

Compound **4** (1 g, 2.01 mmol) was dissolved in anhydrous 1, 6-dioxane under a nitrogen atmosphere, and trimethylbromosilane was added dropwise. The reaction was stirred at 25 °C with nitrogen for 24 h. The solvent is then distilled off under reduced pressure and the residue is dissolved in methanol (30 mL). Next, distilled water was added with stirring until the solution becomes opaque, and it was stirred overnight. The product was filtered and washed with water to obtain a white dry solid (0.51 g, 58% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.59 (s, 2H), 7.79 (d,  $J = 8.4$  Hz, 2H), 7.59 (d,  $J = 8.6$  Hz, 2H), 7.54 (d,  $J = 3.8$  Hz, 2H), 7.50 (d,  $J = 4.2$  Hz, 2H), 7.16 (m, 2H), 4.58 (m, 2H), 2.08 (m, 2H).  $^{13}\text{C}$  NMR (100 Hz,  $\text{DMSO}-d_6$ ):

$\delta$  144.63, 139.44, 128.33, 125.53, 124.34, 124.25, 122.83, 122.46, 117.77, 109.75, 37.72, 27.83, 26.96.

## 2. Synthesis of C-2PACz



Scheme 2. Synthetic route to C-2PACz

### 9-(2-bromoethyl)-3,6-diphenyl-9H-carbazole (III):

3, 6-dibromo-9-(2-bromoethyl)-9H-carbazole (**2**) (1 g, 2.32 mmol), phenylboric acid (2.5 eq.), and  $\text{aq. Na}_2\text{CO}_3$  (2 M, 8 eq.) were dissolved in tetrahydrofuran (20 mL), and the solution was degassed with bubbled nitrogen for 20 min before  $\text{Pd}(\text{PPh}_3)_4$  (0.074 g, 0.066 mmol) was quickly added. The reactants were heated at  $100^\circ\text{C}$  with stirring for 24 hours. Thereafter, the organic solvent was removed under pressure, and the water phase was extracted by ethyl acetate. The organic layer was dried by anhydrous  $\text{Mg}_2\text{SO}_4$ , concentrated, and purified by column chromatography to give the product as a white solid (0.86 g, 87% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.35 (d,  $J = 1.98$  Hz, 2H), 7.75-7.71 (m, 6H), 7.50-7.47 (m, 6H), 7.35 (m, 2H), 4.74 (t,  $J = 7.2$  Hz, 2H), 3.73 (t,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  141.84, 139.94, 133.36, 128.84, 127.33, 126.66, 125.69, 123.86, 119.13, 108.88, 44.93, 28.19.

### diethyl (2-(3,6-diphenyl-9H-carbazol-9-yl)ethyl)phosphonate (IV):

Compound **III** (1 g, 2.34 mmol) was dissolved in triethylphosphite, and the reaction mixture

was heated at reflux for 24h. After the reaction is complete, the solvent is distilled off under reduced pressure. The crude product was purified by column chromatography (acetone: petroleum ether, 1:4) to obtain a transparent liquid (1.05 g, 92.7% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.35 (d, *J* = 1.8 Hz, 2H), 7.76-7.72 (m, 6H), 7.51-7.46 (m, 6H), 7.35 (t, *J* = 7.4 Hz, 2H), 4.65 (m, 2H), 4.10 (m, 4H), 2.32 (m, 2H), 1.29 (m, 6H). <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 141.93, 139.71, 133.05, 128.81, 127.29, 126.58, 125.59, 123.86, 119.07, 108.94, 61.99, 37.24, 25.88, 24.96, 16.38.

**(2-(3,6-diphenyl-9H-carbazol-9-yl)ethyl)phosphonic acid (C-2PACz)**

Compound **IV** (1 g, 2.07 mmol) was dissolved in anhydrous 1, 6-dioxane (20 mL) under a nitrogen atmosphere, and trimethylbromosilane was added. The reaction was stirred at 25 °C for 24 h. Most of the solvent was then distilled off under reduced pressure and the liquid residue was dissolved in methanol (30 mL). Next, distilled water was added with stirring until the solution becomes opaque, and the mixture was stirred overnight. The product is filtered and washed with water to obtain a white dry solid (0.62 g, 70% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 8.69 (s, 2H), 7.84 (m, 6H), 7.70 (br, 2H), 7.54 (m, 4H), 7.39 (m, 2H), 4.68 (m, 2H), 2.15 (m, 2H). <sup>13</sup>C NMR (100 Hz, DMSO-*d*<sub>6</sub>): δ 140.96, 139.49, 131.49, 128.82, 126.62, 126.47, 124.95, 123.23, 118.86, 109.50, 37.76, 27.08.

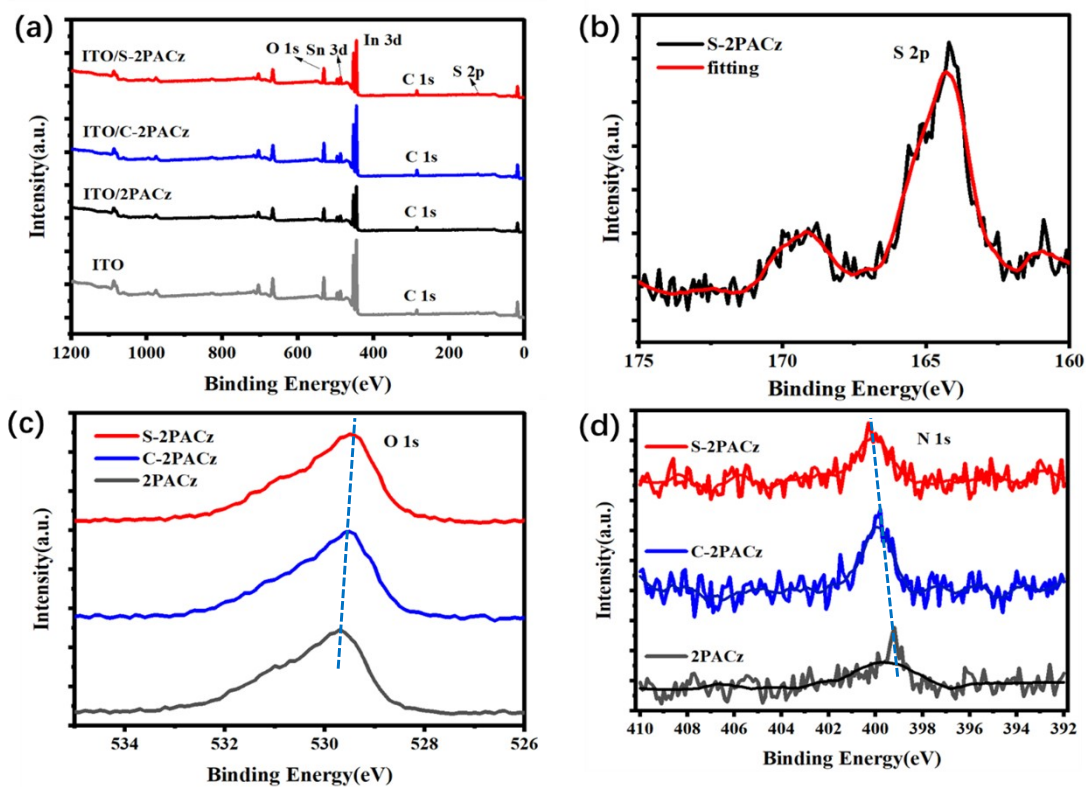
**Table S1. Detailed calculation of cost for the synthesis of 1 g S-2PACz<sup>a</sup>.**

Chemicals of step1		Price (¥/kg)	Dosage (g/g product)	Cost (¥/g product)	Total cost (¥/g product)
Category	Name				

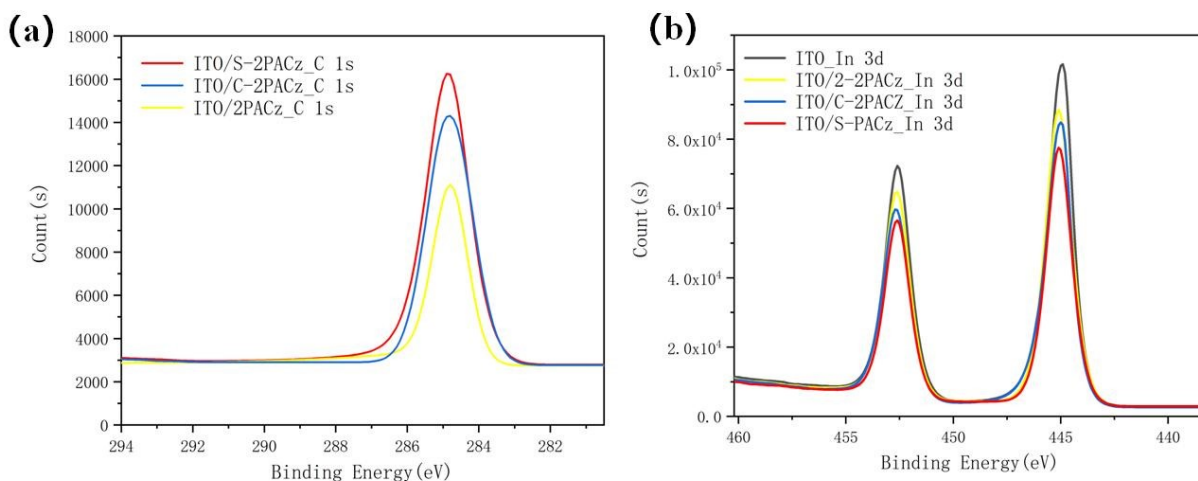
Reaction reagent	3, 6-dibromo-9H-carbazole	900	0.95	0.86	30.9	
	1, 2-dibromoethane	170	41	6.97		
	butylammonium bromide	90	0.094	0.008		
	KOH	50	26	1.3		
Workup	ethyl acetate	11.8	80	0.94		
	Mg <sub>2</sub> SO <sub>4</sub>	96	3	0.29		
Column chromatography	petroleum ether	16.6	600	9.96		
	ethyl acetate	11.8	50	0.59		
	silica gel	20	500	10		
<b>Chemicals of step2</b>		Price (¥/kg)	Dosage (g/g product)	Cost (¥/g product)		Total cost (¥/g product)
Category	Name					
Reaction reagent	product of step 1	30900	1.15	35.54	76.7	
	2-(tributyltin) thiophene	5800	2.16	12.53		
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	68670	0.087	5.97		
	toluene	50	17.4	0.87		
Workup	ethyl acetate	11.8	80	0.94		
	Mg <sub>2</sub> SO <sub>4</sub>	96	3	0.29		
Column chromatography	petroleum ether	16.6	600	9.96		
	ethyl acetate	11.8	50	0.59		
	silica gel	20	500	10		
<b>Chemicals of step3</b>		Price (¥/kg)	Dosage (g/g product)	Cost (¥/g product)		Total cost (¥/g product)
Category	Name					
Reaction reagent	product of step 2	76700	0.98	75.17	102.41	
	triethylphosphite	110	14.1	1.55		
Workup	ethyl acetate	11.8	100	1.18		
	Mg <sub>2</sub> SO <sub>4</sub>	96	3	0.29		
Column chromatography	petroleum ether	16.6	800	13.28		
	ethyl acetate	11.8	80	0.94		
	silica gel	20	500	10		
<b>Chemicals of step4</b>		Price (¥/kg)	Dosage (g/g product)	Cost (¥/g product)		Total cost (¥/g product)
Category	Name					
Reaction reagent	product of step 3	102410	1.96	200.72		233
	trimethylbromosilane	850	4.90	4.16		
	dioxane	120	13	1.56		
	methanol	27.5	24	0.66		
Workup	ethyl acetate	11.8	100	1.18		
	Mg <sub>2</sub> SO <sub>4</sub>	96	3	0.29		
Column chromatography	petroleum ether	16.6	800	13.28		
	ethyl acetate	11.8	80	0.94		
	silica gel	20	500	10		

<sup>a</sup>Herein, we present a rough cost estimate of 1 gram of the S-2PACz. Prices for 1kg of each reagent were collected from chemical suppliers (Adamas, Aladdin, Bidepharm, etc.). For all

synthetic steps, the quantities of reactant and solvents including materials used for the workup and purification are summarized, but waste treatment and energy consumption were not included.



**Figure S1.** X-ray photoelectron spectra of bare and SAM covered ITO:(a) full spectra, (b) S 2p, (c) O 1s, (d) N 1s region.



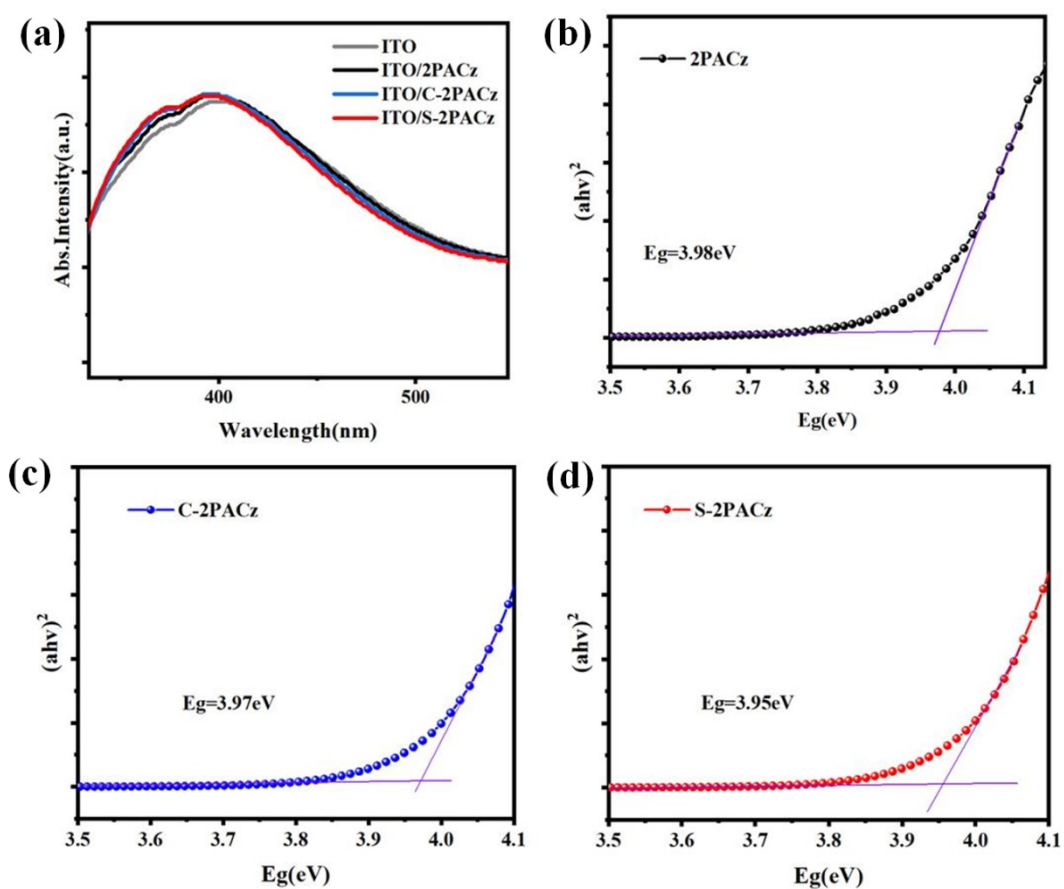
**Figure S2.** XPS C 1s core level spectra (a) and In 3d core level spectra (b) of bare ITO, 2PACz-, C-2PACz-, and S-2PACz-covered ITO.

To calculate a coverage-factor (see Table S2), the modelled area of C 1s was first divided by the number of carbon atoms in the respective SAM molecule and then normalized to the In  $3d_{3/2}$  core level area.

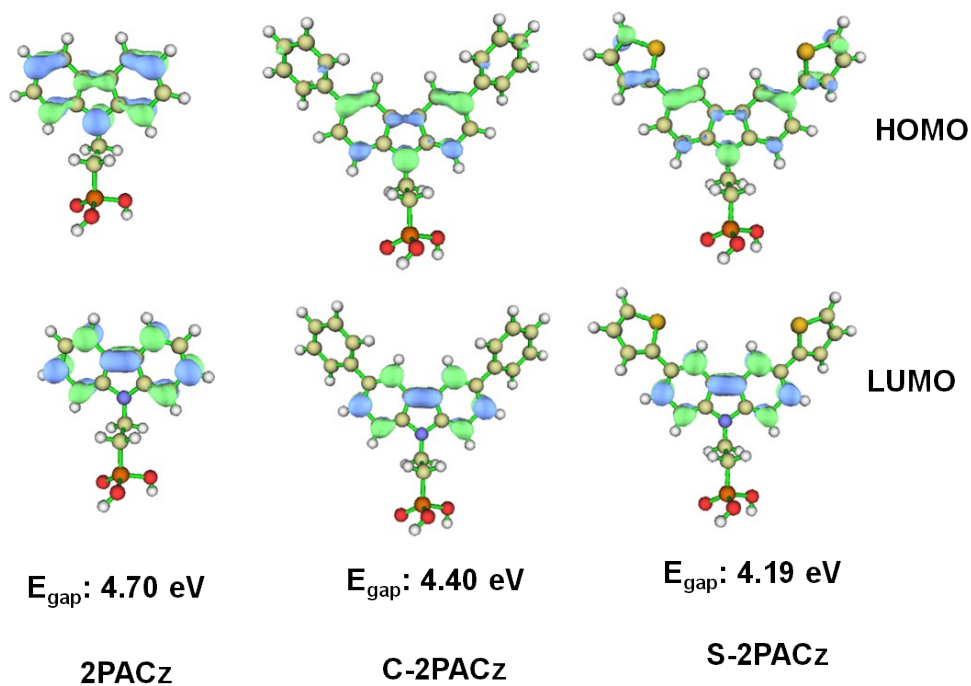
**Table S2.** C 1s and In  $3d_{3/2}$  core-level peak area as measured by XPS for different SAM on ITO-covered glass substrate. The C 1s peak area is divided by the number of carbon atoms and a relative coverage factor is calculated by normalizing to the In  $3d_{3/2}$  core level area.

SAM	C 1s area	In $3d_{3/2}$ area	#Carbon atoms	Coverage factor
ITO/2PACz	9980.66	259503.8	14	$2.7 \times 10^{-3}$
ITO/C- 2PACz	16470.21	221095.05	26	$2.9 \times 10^{-3}$
ITO/S-2PACz	23641.8	201145.32	22	$4.5 \times 10^{-3}$

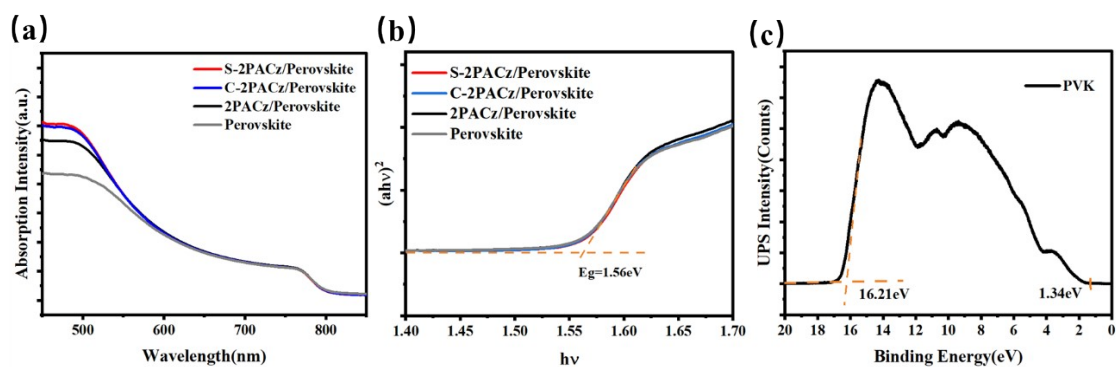




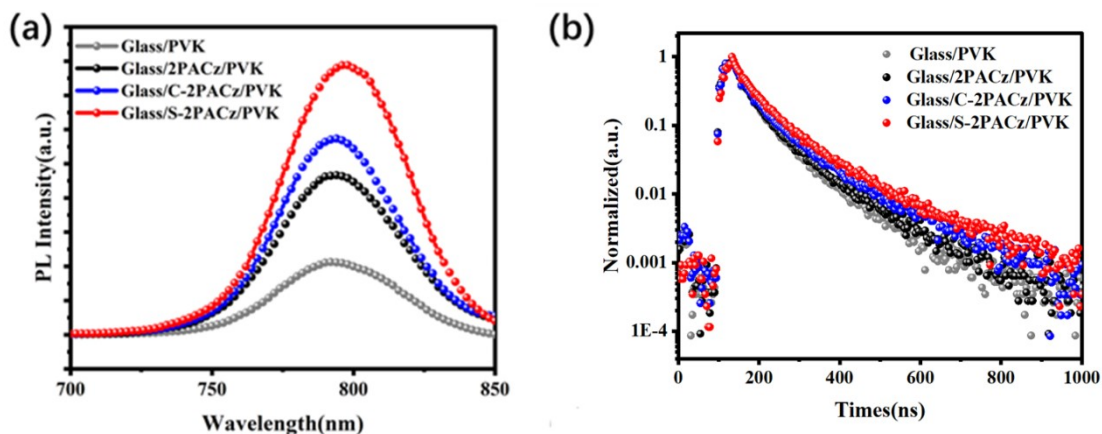
**Figure S3.** (a) The magnified absorption spectra region adopted from Figure 2a. (b-d) Tauc plots of different SAMs and the determined bandgaps.



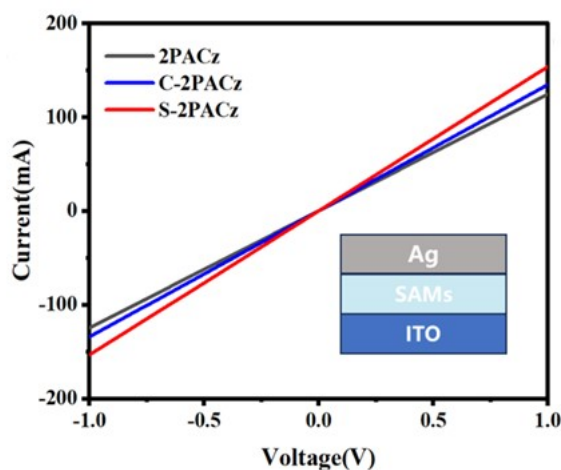
**Figure S4.** The calculated bandgaps and HOMO and LUMO orbitals.



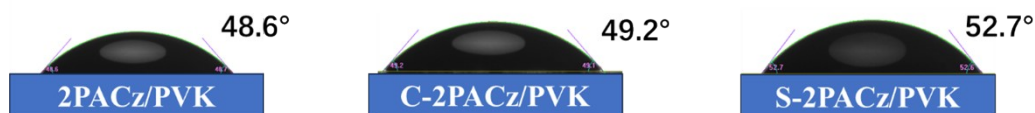
**Figure S5.** (a) UV-vis absorption spectra and the relevant Tauc-plot curves (b) of the perovskite films. (c) UPS spectra of perovskite film.



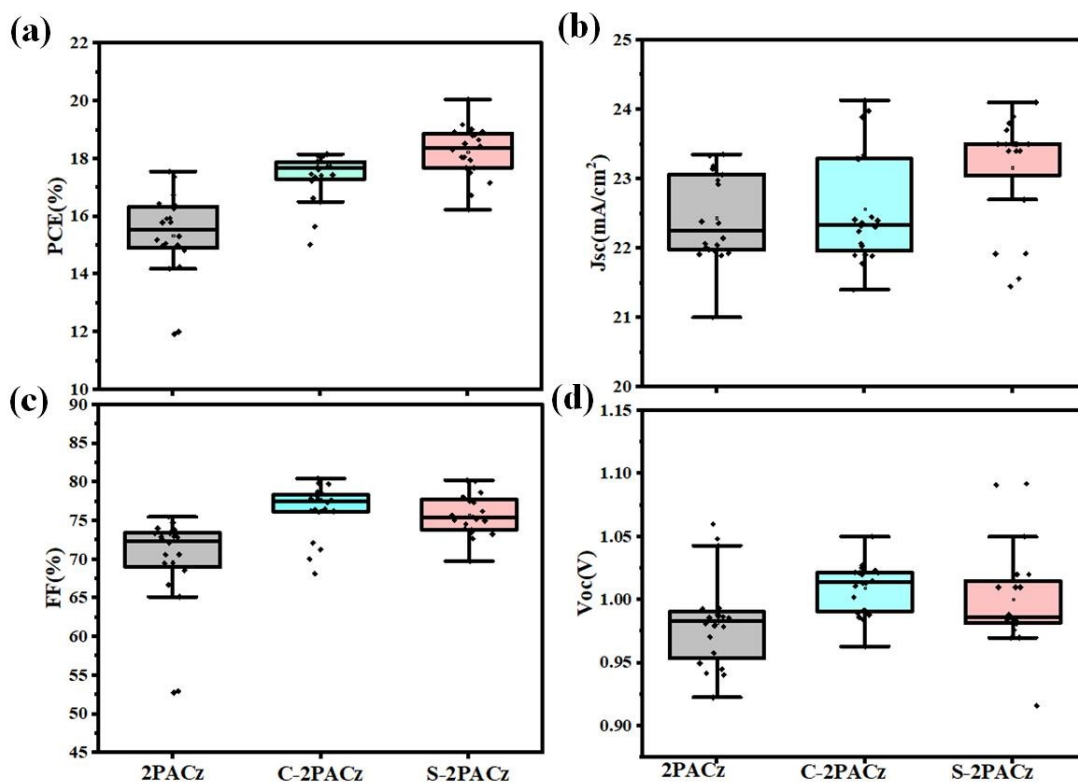
**Figure S6.** Photoluminescence (PL) (a) and time-resolved photoluminescence (TRPL) (b) spectra of perovskite thin films deposited on quartz, quartz/2PACz, quartz/C-2PACz, and quartz/S-2PACz.



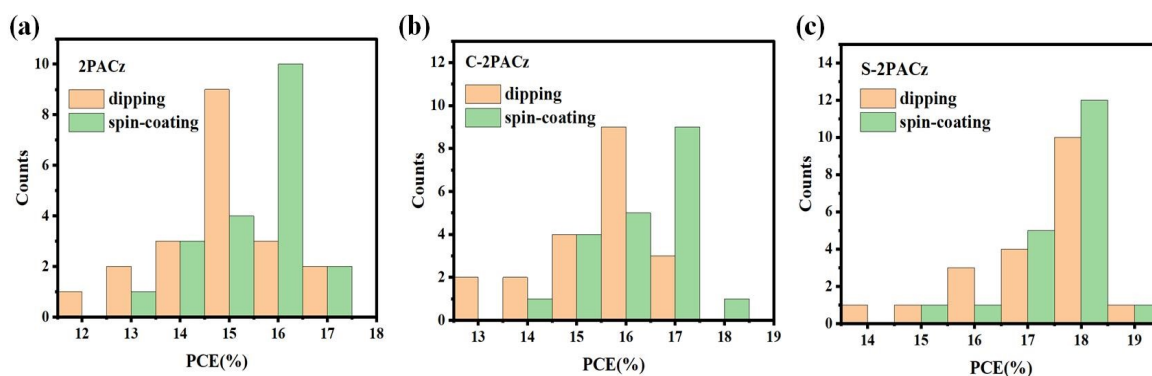
**Figure S7.** Dark I-V curves across the various ITO/SAMs/Ag structure for determining the resistance and conductivities of the HSLs.



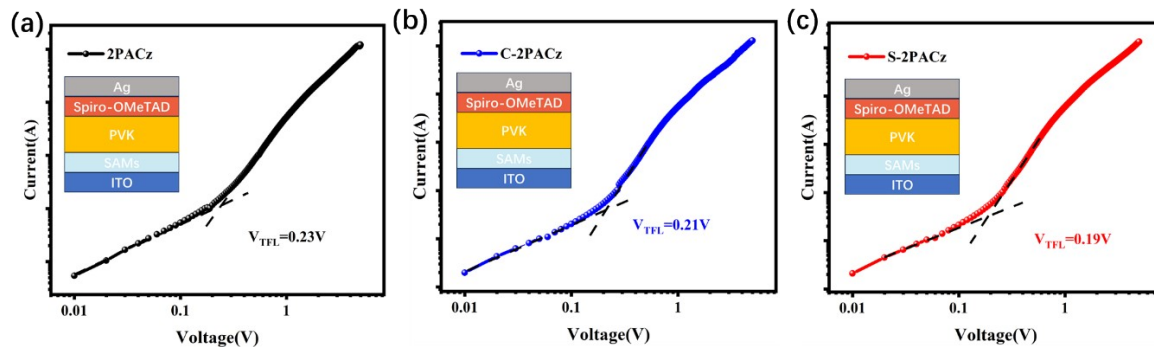
**Figure S8.** Water contact angles of perovskite thin films coated on 2PACz, C-2PACz, and S-2PACz.



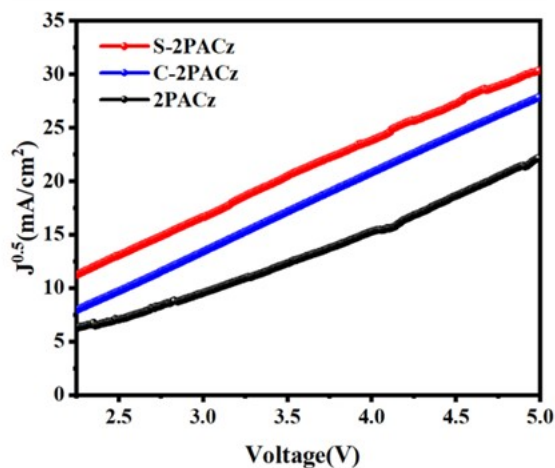
**Figure S9.** Statistical distributions of (a) power conversion efficiency (PCE), (b) short-circuit current density ( $J_{sc}$ ), (c) fill factor (FF), and (d) open circuit voltage ( $V_{oc}$ ) of perovskite solar cells with different SAMs.



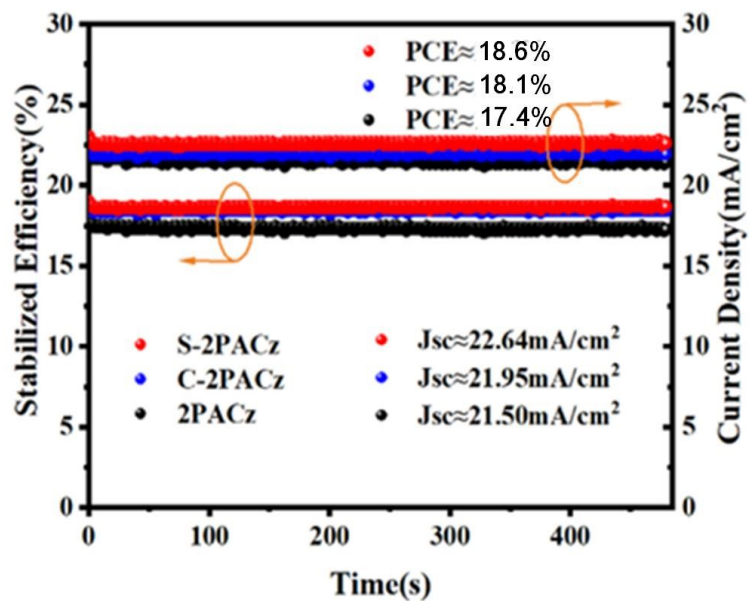
**Figure S10.** Statistical comparisons of PCEs between PSCs with SAMs from spin-coating (without washing) and dipping (with subsequent washing). The SAM-modified ITO substrates were either prepared by spin-coating a 0.3 mg/mL SAM solution at 4000 rpm for 30 s followed by subsequent heating at 100 °C for 10 min, or were dipped into a SAM solution (0.3 mg/mL concentration in DMSO) for 4 hours at room temperature followed by subsequent washing.



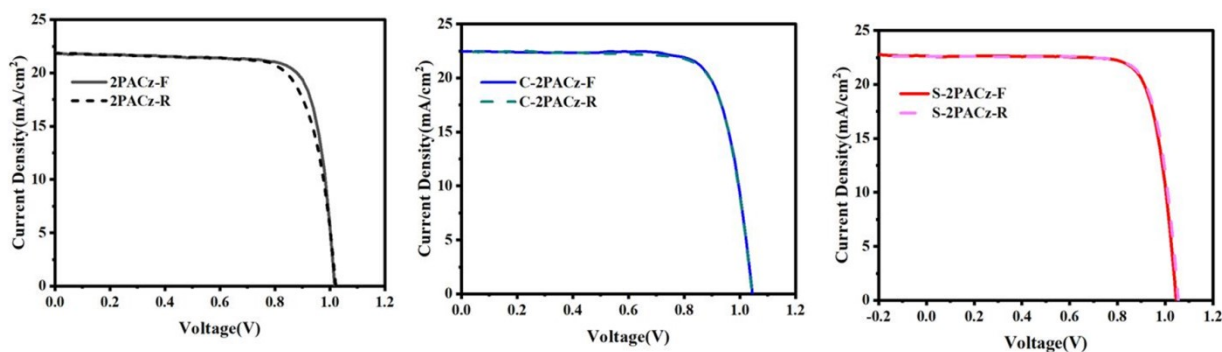
**Figure S11.** Dark  $J$ - $V$  curves of hole-only device with different HTLs. The structure of hole only device is ITO/SAMs/Perovskite/Spiro-OMeTAD/Ag.



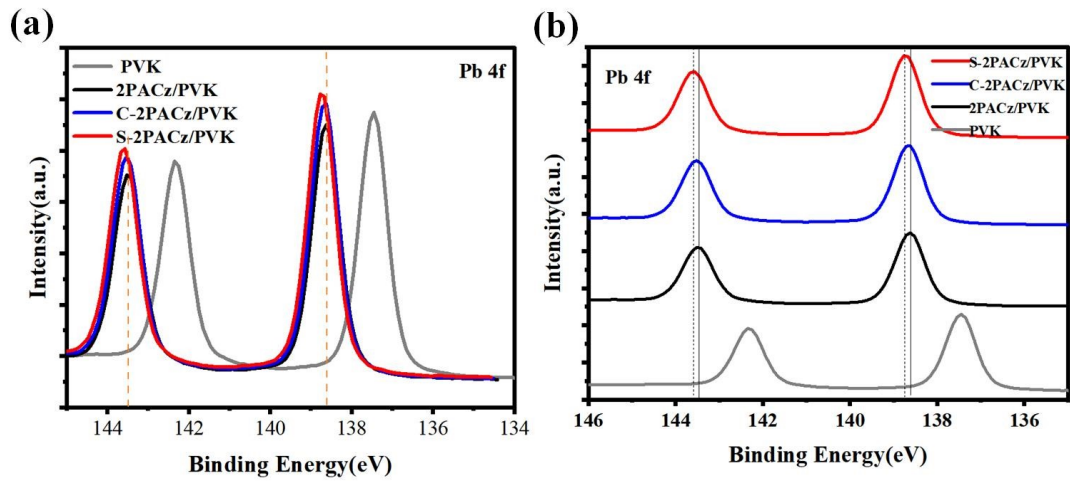
**Figure S12.**  $J^{0.5}$ - $V$  curves of hole-only device with different HTLs. The structure of devices is ITO/SAMs/Perovskite/Spiro-OMeTAD/Ag.



**Figure S13.** Steady-state power output at the MPP of the champion device based on self-assemble molecule modified substrate.



**Figure S14.** (a-c)  $J-V$  curves of the best performing PSCs with forward and reverse scans under simulated AM 1.5G illumination.



**Figure S15.** XPS spectra of Pb 4*f* orbitals of the pristine perovskite films and those with the SAMs. Different illustrative styles are provided.

**Table S3.** The parameters of UPS spectra.

Sample	$E_{\text{cut-off}}$ (eV)	$E_{\text{F}}$ (eV)	$E_{\text{F,edge}}$ (eV)	$E_{\text{VB}}$ (eV)	$E_{\text{g}}$ (eV)	$E_{\text{CB}}$ (eV)
<b>2PACz</b>	16.81	4.41	1.03	5.44	3.98	1.46
<b>C-2PACz</b>	16.76	4.46	1.00	5.46	3.97	1.49
<b>S-2PACz</b>	16.74	4.48	1.00	5.48	3.95	1.53
<b>PVK</b>	16.21	5.01	1.34	6.35	1.56	4.79

**Table S4. TRPL parameters of perovskite thin films.**

Sample	$\tau_1(\text{ns})$	$\tau_2(\text{ns})$	$A_1(\%)$	$A_2(\%)$	$\tau_{ave}(\text{ns})$
GLASS/PVK	25.43	84.27	78.5%	21.5%	53.42
GLASS/2PACz/PVK	25.81	93.90	78.6%	21.4%	59.69
GLASS/C-2PACz/PVK	28.27	100.50	79.0%	21.2%	63.36
GLASS/S-2PACz/PVK	33.87	107.20	79.2%	20.8%	67.15
ITO/PVK	17.47	45.06	38.9%	61.1%	39.60
ITO/2PACz/PVK	13.76	40.08	72.5%	27.5%	27.58
ITO/C-2PACz/PVK	12.70	36.97	65.1%	34.9%	27.50
ITOS-2PACz/PVK	9.35	26.22	84.7%	15.3%	15.02

The average lifetime is calculated using the equation<sup>3</sup>:

$$\tau_{ave} = \frac{\sum_{i=1}^n A_i \tau_i^2}{\sum_{i=1}^n A_i \tau_i}$$

**Table S5. EIS fitting parameters.**

Sample	$R_s(\Omega)$	$C_{rec}$	$R_{rec}(\Omega)$
2PACz/PVK	2.745	$1.16 \cdot 10^{-7}$	956.6
C-2PACz/PVK	2.877	$1.15 \cdot 10^{-7}$	1702
S-2PACz/PVK	3.720	$1.15 \cdot 10^{-7}$	2551



**Table S6. Summary of  $J$ - $V$  parameters of PSCs with different SAMs.**

HTLs		$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
<b>2PACz</b>	F-sweep	21.87	1.02	79.01	17.50
	R-sweep	21.82	1.02	75.51	16.75
<b>C-2PACz</b>	F-sweep	22.45	1.05	77.37	18.16
	R-sweep	22.43	1.04	77.07	18.05
<b>S-2PACz</b>	F-sweep	22.66	1.05	78.65	18.65
	R-sweep	22.60	1.06	78.79	18.79

## References

1. Zhang, J.; Lu, T. Efficient evaluation of electrostatic potential with computerized optimized code. *Phys. Chem. Chem. Phys.* **2021**, *23* (36), 20323-20328.
2. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.
3. Jiang, W.; Li, F.; Li, M.; Qi, F.; Lin, F. R.; Jen, A. K.-Y.  $\pi$ -Expanded Carbazoles as Hole-Selective Self-Assembled Monolayers for High-Performance Perovskite Solar Cells. *Angew. Chem. Int. Ed.* **2022**, *61* (51), e202213560.