

# Supporting Information

## **All Perovskite Tandem Solar Cells Approach 26.5% Efficiency by Employing Wide Bandgap Lead Perovskite Solar Cells with New Mono-molecular HTL Layer**

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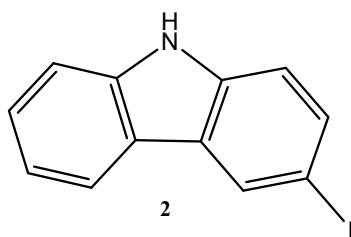
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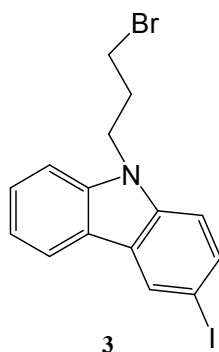
## EXPERIMENTAL SECTION

*Materials:* All chemical reagents were used as received without further purification. Xi'an Polymer Light Technology Corp. supplied PTAA. FAI, CsI, PbBr<sub>2</sub>, PbI<sub>2</sub> purchased from Advanced Election Technology CO., Ltd. Guanidine bromide, FABr and 2PACz from Tokyo Chemical Industry Co., Ltd. Sigma Aldrich provided CsBr, EDA, SnI<sub>2</sub>, SnF<sub>2</sub>, GuASCN, BCP, and C60. All solvents were purchased from Sigma Aldrich. PEDOT-PSS aqueous solution (Al 4083) was purchased from Heraeus Clevios. 4dp3PACz were synthesized according to the description in Experimental Section and Figure 1a. 9H-Carbazole, 1,3-dibromopropane, triethylphosphite, 4-(diphenylamino)phenylboronic acid, 2-methoxy-3-pyridinylboronic acid, bis(triphenylphosphine)palladium(II) dichloride, KOH, K<sub>2</sub>CO<sub>3</sub>, Cu, CuI, 18-crown-6, 1,4-dioxane, acetone, dimethylformamide, and tetrahydrofuran were purchased from Aldrich and used as received.

### *Experimental details of the synthesis*

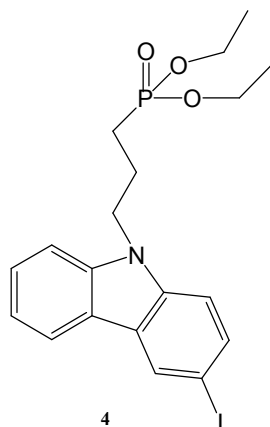


3-Iodo-9H-carbazole (2) was synthesized from commercially available 9H-carbazole by Tucker iodination with KI/KIO<sub>3</sub> in acetic acid.[1]

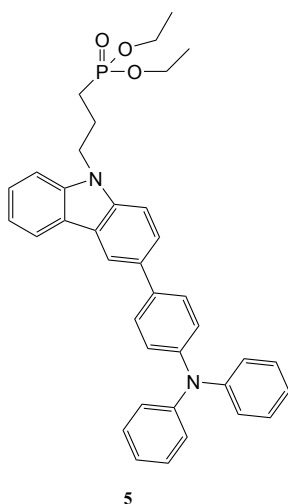


9-(3-bromopropyl)-3-iodo-9H-carbazole (3) was obtained by a standard alkylation reaction of 3-iodo-9H-carbazole using 1,3-dibromopropane as the alkylation agent and KOH as the base.[2] MS (APCI+, 20 V): 413.53 ([M+H], 100%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>6</sub>, δ): 8.42 (s, 1H, Ar), 8.05 (d, 1H, J = 7.6 Hz, Ar), 7.74 (d, 1H, J = 8.8 Hz, Ar), 7.54-7.48 (m, 2H, Ar), 7.32-7.27 (m, 2H, Ar), 4.49 (t, 2H, J = 6.8, CH<sub>2</sub>), 3.38 (t, 2H, J = 6 Hz, CH<sub>2</sub>), 2.51-

2.36 (m, 2H, CH<sub>2</sub>).

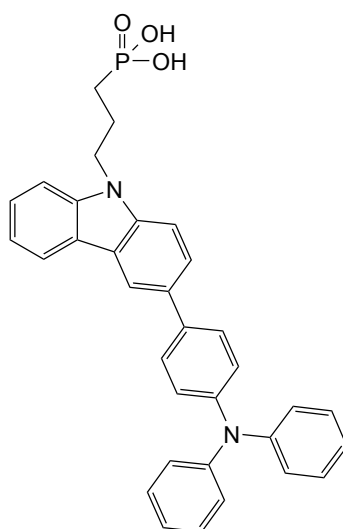


Diethyl [3-(3-iodo-9*H*-carbazol-9-yl)propyl]phosphonate (4). 9-(3-bromopropyl)-3-iodo-9*H*-carbazole **3** (2 g, 4.84 mmol) was dissolved in triethylphosphite (2.48 ml), and the reaction mixture was heated at reflux for 24 h. After TLC control, the crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 2:1) as an eluent—yield: 1.5 g of (75%) colorless resin. MS (APCI+, 20 V): 472.27 ([M+H], 100%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ): 8.56 (s, 1H, Ar), 8.20 (d, 1H, J = 7.6 Hz, Ar), 7.72 (d, 1H, J = 8.4 Hz, Ar), 7.66 (d, 1H, J = 8 Hz, Ar), 7.55-7.43 (m, 2H, Ar), 7.22 (t, 1H, J = 7.2 Hz, Ar), 4.47 (t, 2H, J = 7.8 Hz, NCH<sub>2</sub>), 4.02-3.91 (m, 4H, 2x CH<sub>2</sub>), 1.99-1.89 (m, 2H, CH<sub>2</sub>), 1.78-1.70 (m, 2H, CH<sub>2</sub>), 1.22-1.14 (m, 6H, 2x CH<sub>3</sub>).



Diethyl [3-[3-[4-(diphenylamino)phenyl]-9*H*-carbazol-9-yl]propyl]phosphonate (5). 0.50 g (1.06 mmol) of diethyl 3-(3-iodo-9*H*-carbazol-9-yl) propyl phosphonate **5**, 0.46 g (1.59 mmol) of 4-(diphenylamino)phenylboronic acid, 0.03 g (0.07 mmol) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 0.29 g (5.16 mmol) of powdered potassium hydroxide was stirred in 7

ml of THF containing degassed water (0.7 ml) at reflux under nitrogen for 3 h. After TLC control, the reaction mixture was poured into iced water, and chloroform extracted the product. The organic fraction was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 4:1) as an eluent—yield: 0.4 g (80 %) of colorless resin. MS (APCI+, 20 V): 589.68 ([M+H], 100%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$ ): 8.37 (s, 1H, Ar), 7.91-7.63 (m, 7H, Ar), 7.44 (t, 2H,  $J = 8$  Hz, Ar), 7.34-7.27 (m, 4H, Ar), 7.18 (t, 1H,  $J = 7.6$  Hz, Ar), 7.14-6.95 (m, 6H, Ar), 4.48 (t, 2H,  $J = 7.8$  Hz,  $\text{NCH}_2$ ), 4.06-3.94 (m, 4H, 2x  $\text{OCH}_2$ ), 1.96-1.84 (m, 2H,  $\text{CH}_2$ ), 1.76-1.72 (m, 2H,  $\text{CH}_2$ ), 1.22-1.10 (m, 6H, 2x  $\text{CH}_3$ ).



4dp3PACz

3-[3-[4-(diphenylamino)phenyl]-9H-carbazol-9-yl]propylphosphonic acid (4dp3PACz). Diethyl [3-[3-[4-(diphenylamino)phenyl]-9H-carbazol-9-yl]propyl]phosphonate 5 (0.4 g, 0.67 mmol) was dissolved in anhydrous 1,4-dioxane (10 ml) under argon atmosphere followed by dropwise addition of bromotrimethylsilane (1.43 ml, 10.84 mmol); the reaction was stirred for 24 h at 25 °C. Afterward, methanol (10 ml) was added, and stirring continued for 3 h. Finally, distilled water was added dropwise (20 ml) until the solution became opaque and stirred overnight. The precipitated product was filtered off and washed with water to give 0.32 g (80 %) of bright powder (80 %). MS (APCI+, 20 V): 533.19 ([M+H], 100%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$ ): 8.43 (s, 1H, Ar), 7.80-7.61 (m, 7H, Ar), 7.45 (t, 2H,  $J = 8$  Hz, Ar), 7.32-7.29 (m, 4H, Ar), 7.21 (t, 1H,  $J = 7.6$  Hz, Ar), 7.16-6.99 (m, 6H, Ar), 4.48 (t, 2H,  $\text{CH}_2$ ), 2.01-1.95 (m, 2H,  $\text{CH}_2$ ), 1.59-1.51 (m, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR

(100 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 151.92, 147.71, 146.26, 143.60, 140.95, 139.81, 139.67, 136.82, 136.77, 136.16, 132.70, 131.90, 131.27, 130.21, 130.03, 128.51, 128.20, 126.39, 125.39, 124.95, 124.56, 124.22, 123.39, 123.18, 122.73, 121.03, 119.35, 118.52, 110.17, 109.93, 34.86, 26.17, 21.51.

*Device Fabrication:* ITO was ultrasonically cleaned with pure water, isopropanol, and acetonitrile for 15 minutes, respectively. Then the ITO substrate was dried and cleaned with plasma for 5 min (electronic Diener, Plasma-surface-technology, Germany). After cooling to room temperature, the ITO was transferred to the glove box. 2PACz monolayer was prepared, according to the previous work,[3] 1mM 2PACz was dissolved in isopropanol (IPA) and stirred at room temperature for 12 hours. Then, 100  $\mu$ L of the 2PACz solution was dropped on the ITO and spin-coated at 2000 rpm for 30 s. The sample was heated at 100 °C for 10 min. The sample was washed with IPA by spin-coating to remove the unbonded 2PACz molecules from the ITO surface, then heated at 100 °C for 1 min. 4dp3PACz monolayer was prepared as follows: 4dp3PACz was dissolved in DMF and stirred at room temperature for 10 hours to prepare 1 mM solution. Then, 100  $\mu$ L 4dp3PACz was dropped on the ITO substrate and spin-coated at 2000 rpm for 30 s. The sample was heated at 100 °C for 10 min. The sample was washed with IPA by spin-coating to remove the unbonded 4dp3PACz molecules from the ITO substrate and heated at 100 °C for 1 min. 1.2 M perovskite precursor solution was prepared by dissolving FAI (0.576 mol), CsI (0.144 mol), FABr (0.384 mol), PbI<sub>2</sub> (0.720 mol), PbBr<sub>2</sub> (0.480 mol), and CsBr (0.096 mol) in the 1 mL of DMSO/DMF (1/4, v/v) mixture. Before use, the solution was filtered by a 0.22  $\mu$ m PTFE membrane. The precursor (70  $\mu$ L) was dropped and spin-coated at 2000 rpm for 10 s and 6000 rpm for 40 s to fabricate a perovskite thin film. 150  $\mu$ L chlorobenzene was dropped in the 30s after the spin-coated was started. After that, the sample was heated at 100 °C for 15 min. Guanidine bromide (GuBr: 0.5 mg/mL in IPA) was spin-coated at 5000 r.p.m. for the 30s as a modification layer. C60 (20 nm), BCP (7 nm), and Ag (100 nm) were deposited consecutively on the substrate by thermal evaporation under a vacuum of 10<sup>-5</sup> Pa using a shadow mask.

A Tandem perovskite solar cell was fabricated as follows: The WBG PSCs (FA<sub>0.8</sub>Cs<sub>0.2</sub>PbI<sub>1.8</sub>Br<sub>1.2</sub>) were prepared in the same way described above. After depositing

the C60 on the wide bandgap perovskite film, the substrates were transferred to the ALD system to deposit 20 nm SnO<sub>2</sub> at 100 °C. Tetrakis(dimethylamino), tin(iv), and deionized water were used as the precursor. After the ALD-SnO<sub>2</sub> deposition, the substrates were transferred to the magnetron sputtering system to deposit 100 nm IZO on the ALD-SnO<sub>2</sub>. The PEDOT: PSS layer was spin-cast on the IZO, and the sample was annealed at 120 °C for 20 min. Then the narrow bandgap perovskite (Cs<sub>0.025</sub>FA<sub>0.475</sub>MA<sub>0.5</sub>Sn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>2.925</sub>Br<sub>0.075</sub>) was prepared on the PEDOT: PSS layer, according to our previous report.[3] Cs<sub>0.025</sub>FA<sub>0.475</sub>MA<sub>0.5</sub>Sn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>2.925</sub>Br<sub>0.075</sub> precursor solution was obtained by mixing Cs<sub>0.05</sub>FA<sub>0.95</sub>SnI<sub>3</sub> (1.4 M) (228.72 mg of FAI, 521.52 mg of SnI<sub>2</sub>, and CsI of 18.2 mg in 1 ml of DMF: DMSO (4:1, v/v) solution), MAPbI<sub>3</sub> (1.4 M) (222.56 mg of MAI, 645.41 mg of PbI<sub>2</sub>, and 13.23 mg of GuASCN in 1 ml of DMF: DMSO (9:1, v/v) solution) and MAPbBr<sub>3</sub> (1.4 M) (156.76 mg of MABr and 513.82 mg of PbBr<sub>2</sub> in 1 ml of DMF: DMSO (9:1, v/v) solution) in a certain volume ratio.[3] The perovskite precursor was then dropped onto the PEDOT: PSS and spin-coated at 1000 rpm for 10 s, followed by 5000 rpm for 50 s. 750 μL toluene was dropped at the 20s from the beginning. The sample was heated at 100 °C for 5 min. The perovskite layer was then passivated by ethylenediamine (EDA:0.1 mM in toluene) by a spin coating. PCBM (7.5 mg/ml in CB) was coated at 5000 rpm for 50 s. The sample was heated at 75 °C for 5 min. Finally, C60 (20 nm), BCP (7 nm), and Ag (100 nm) were deposited consecutively under vacuum conditions by thermal evaporation to give the tandem perovskite solar cell.

*Characterization:* XRD patterns were obtained by a Rigaku Smartlab X-ray diffractometer. The solar cell measurements were carried out using a Keithley 4200 source meter and a solar simulator under 100mWcm<sup>-2</sup> AM 1.5G in the ambient condition (Bunkouki CEP-2000SRR). The effective active area of the device is defined to be 0.1 cm<sup>2</sup> and 0.04 cm<sup>2</sup> using a black metal mask. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a monochromatic Xenon lamp (Bunkouki CEP-2000SRR). HOMO energy level was obtained from a photoelectron yield measurement system (PYS, BUNKOKEIKI, KV-205 HK) under high vacuum (~10<sup>-4</sup> Pa) conditions. Scanning electron microscopy (SEM, FE-SEM, JEOL JSM-6340) was employed to observe the surface morphology of the perovskite thin film. The photoluminescence (PL) and time-resolved

photoluminescence (TRPL) were measured with Jasco FP6500 Spectrofluorometer. Fermi Level was measured by FAC-2 (RIKEN KEIKI Co., Ltd.). SEM (JPS-9200, JEOL Ltd., Japan) was used to observe the perovskite film surface. Calculations were performed within the Density Functional (DFT) formalism using the Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation functional.[4] All calculations were performed utilizing the CP2K package.[5]

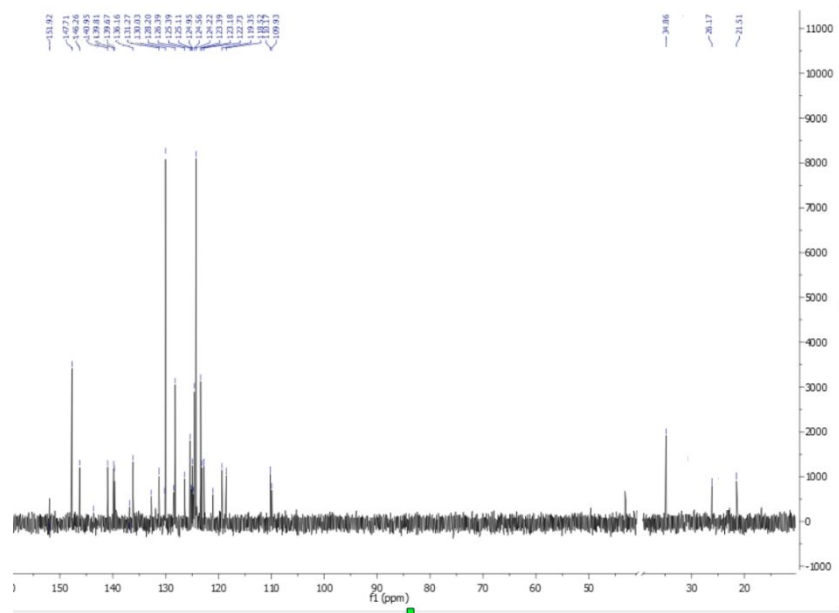


Figure S1.  $^{13}\text{C}$ -NMR spectrum of 4dp3PACz.





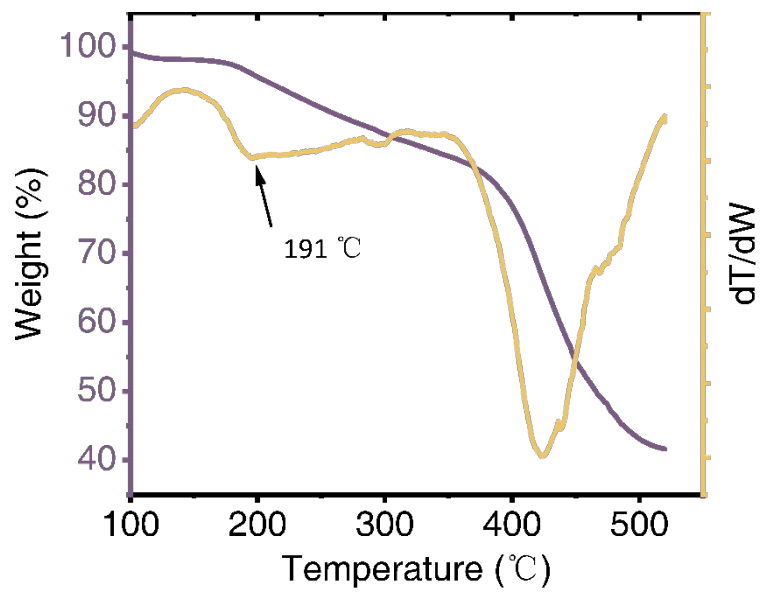


Figure S3. Differential scanning calorimetry result of 4dp3PACz.

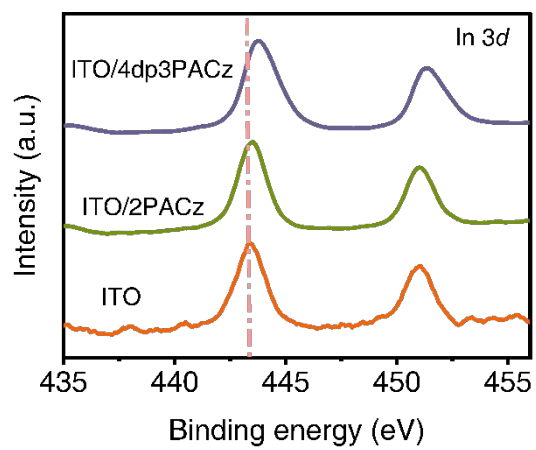


Figure S4. In 3d XPS signal of the ITO with or without 4dp3PACz.

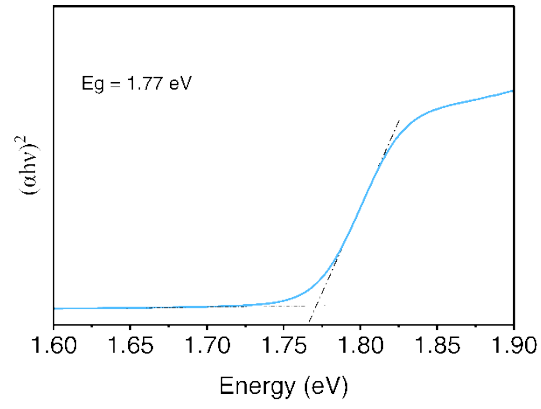


Figure S5. Tauc plot of ITO/4dp3PACz/perovskite to evaluate the bandgap of perovskite.  
(Perovskite composition:  $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.8}\text{Br}_{1.2}$ )

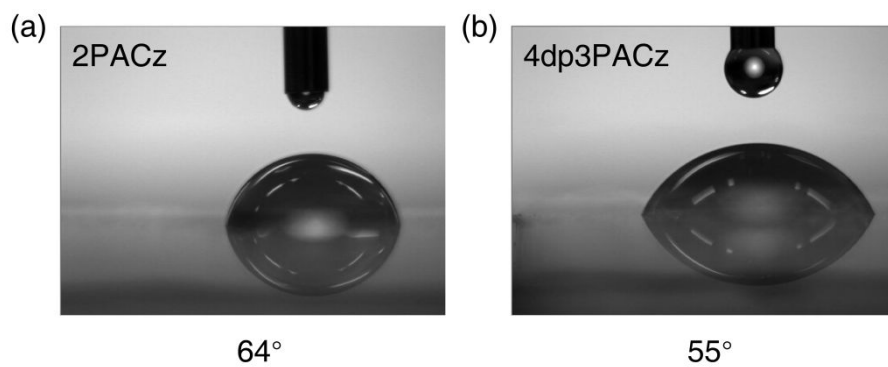


Figure S6. Water contact angle test on (a) ITO/2PACz (64 °) and (b) ITO/4dp3PACz (55 °).

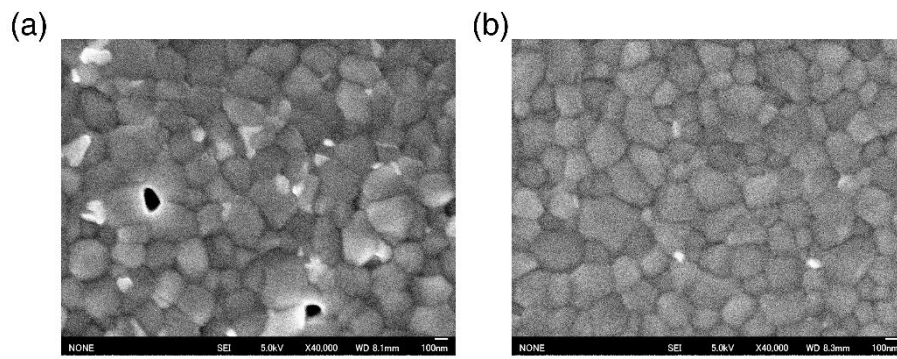


Figure S7. Top-view SEM images of (a) perovskite on ITO/2PACz and (b) perovskite on ITO/4dp3PACz. (Perovskite composition:  $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.8}\text{Br}_{1.2}$ )

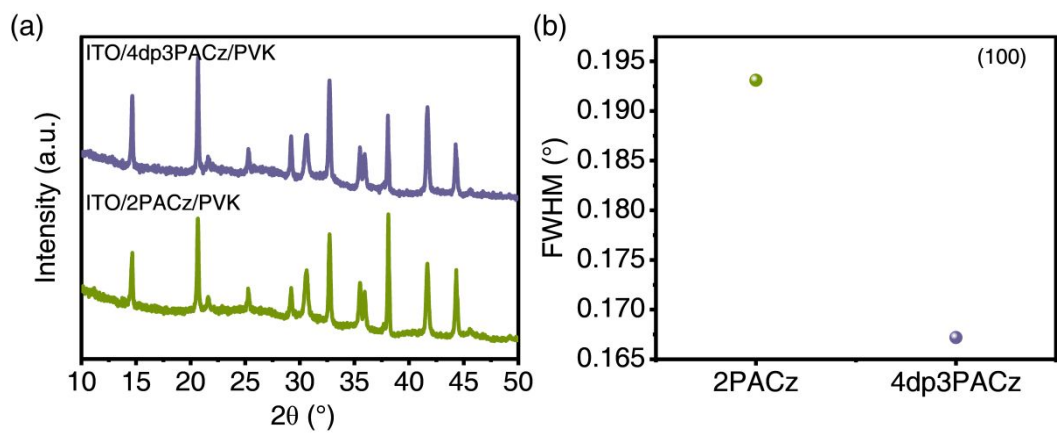


Figure S8. (a) XRD patterns of the perovskite films deposited on ITO/2PACz and ITO/4dp3PACz and FWHM of the perovskite ((100) plane) deposited on ITO/2PACz and ITO/4dp3PACz. (Perovskite composition:  $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.8}\text{Br}_{1.2}$ )

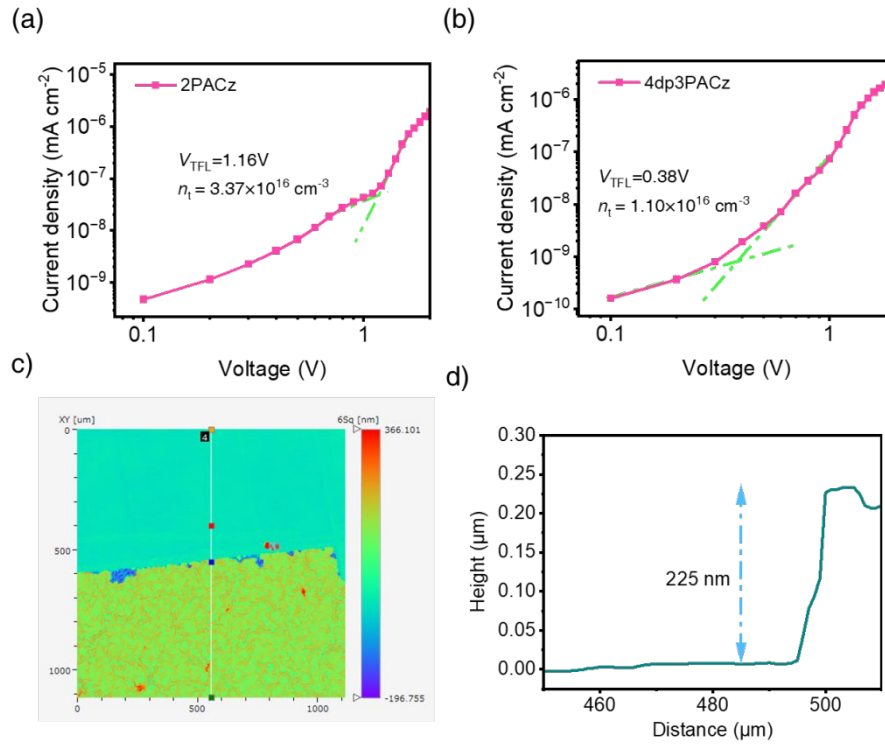


Figure S9. Dark  $I$ - $V$  curves of hole only devices with structure of (a) ITO/2PACz/perovskite/Spiro-OMeTAD/Ag and (b) ITO/4dp3PACz/3,3PrPACz/perovskite/Spiro-OMeTAD/Ag. (Perovskite composition:  $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.8}\text{Br}_{1.2}$ ) (c) and (d) shows the thickness of the perovskite film.



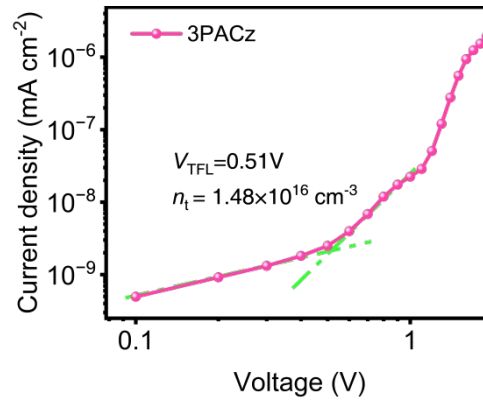


Figure S10. Dark  $I$ - $V$  curves of hole only devices with structure of ITO/3PACz/perovskite/Spiro-OMeTAD/Ag.

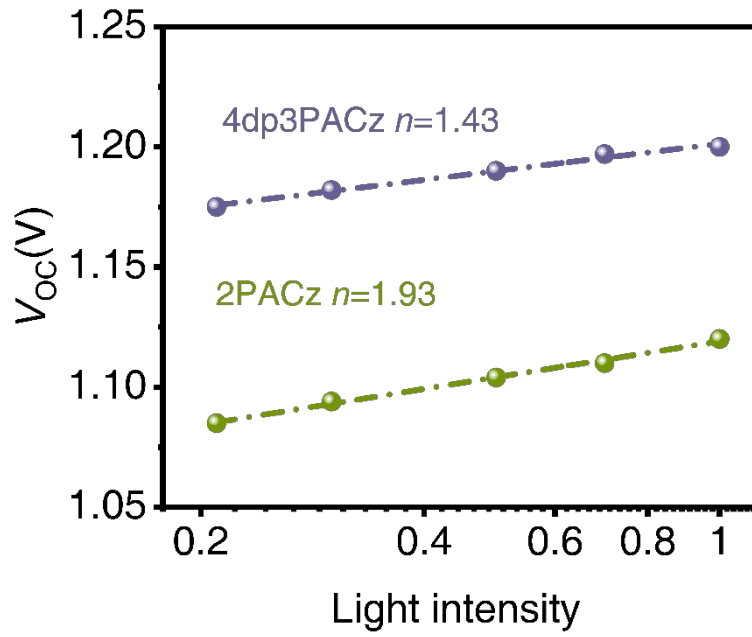


Figure S11.  $V_{OC}$  dependence on light intensity for device with 2PACz- and 4dp3PACz-layer. (Device composition: ITO/SAMs/perovskite/GuBr/C60/BCP/Ag, perovskite composition,  $FA_{0.8}Cs_{0.2}PbI_{1.8}Br_{1.2}$ )

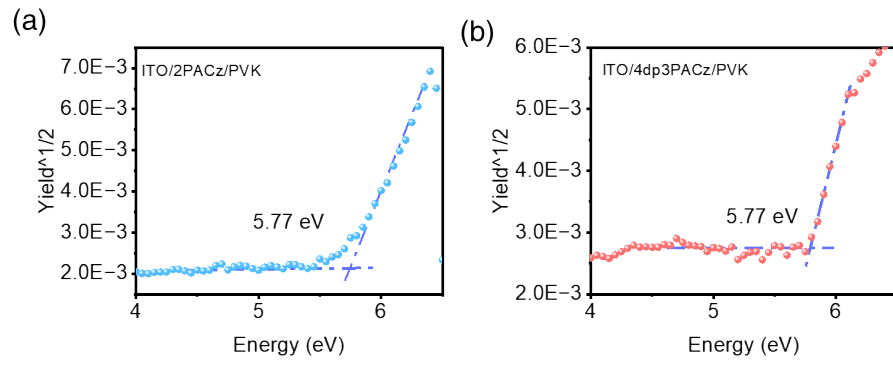


Figure S12. The PYS data of the device with the structure of (a) ITO/2PACz/perovskite and (b) ITO/4dp3PACz/perovskite.

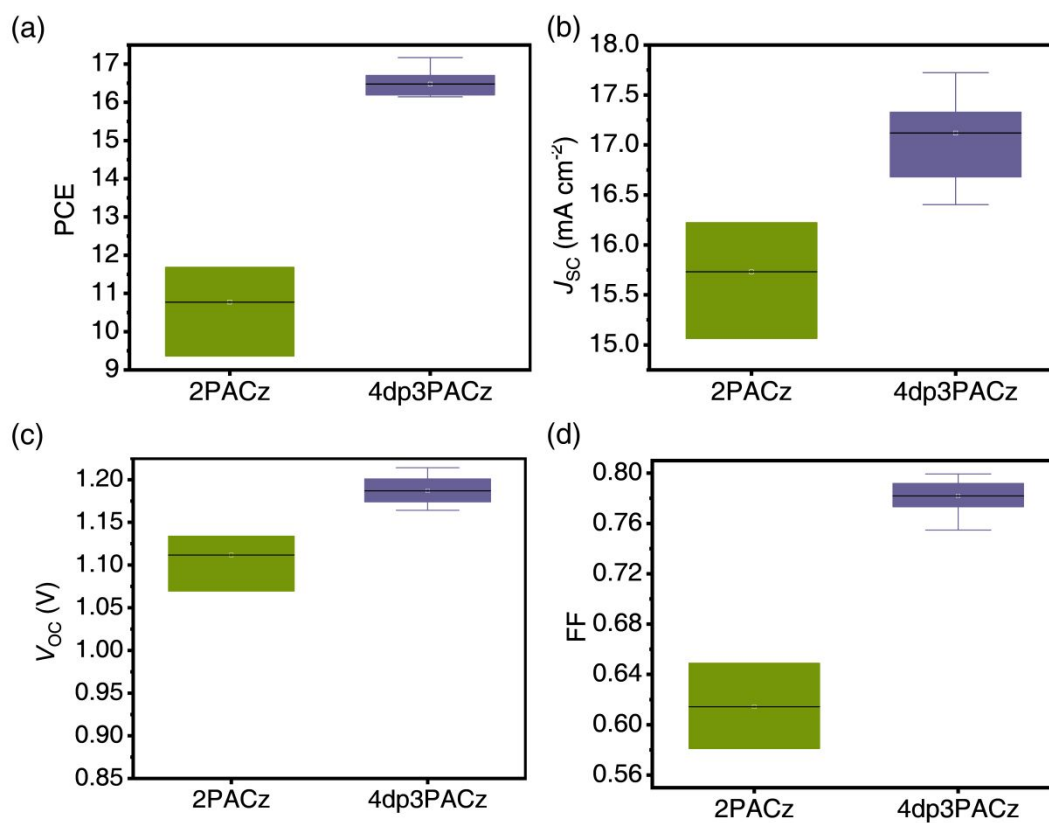


Figure S13. Statistics of (a) PCE, (b)  $J_{sc}$ , (c)  $V_{oc}$ , and (d) FF of perovskite solar cells with 2PACz or 4dp3PACz HTL. (Device composition: ITO/SAMs/perovskite/GuBr/C60/BCP/Ag, perovskite composition, FA<sub>0.8</sub>Cs<sub>0.2</sub>PbI<sub>1.8</sub>Br<sub>1.2</sub>)

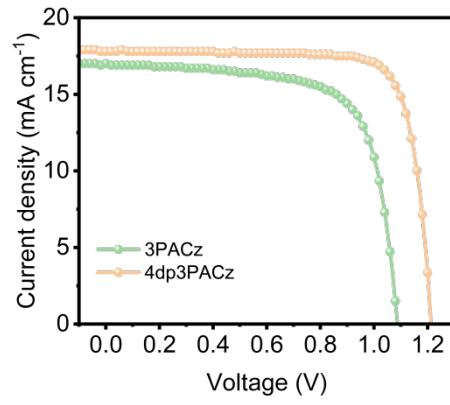


Figure S14. The  $J$ - $V$  curves of the PSCs based on 3PACz or 4dp3PACz as HTL.

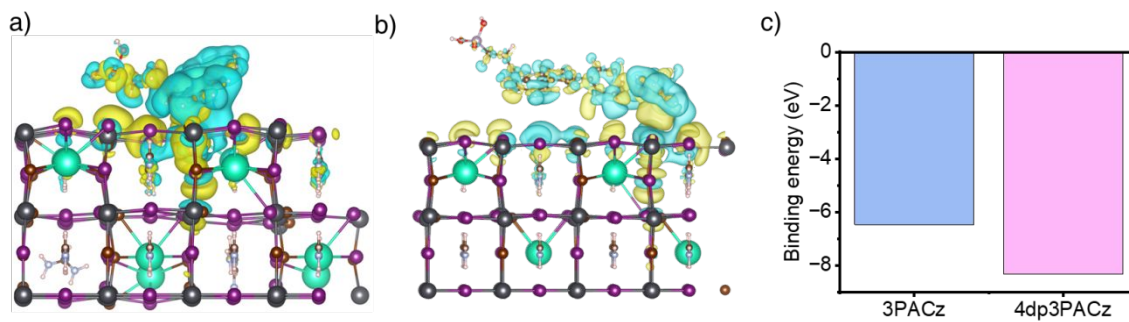


Figure S15. The differential charge density of the system with the structure of (a) 3PACz/perovskite and (b) 4dp3PACz/perovskite. (c) the binding energy of the system corresponding to (a) and (b).

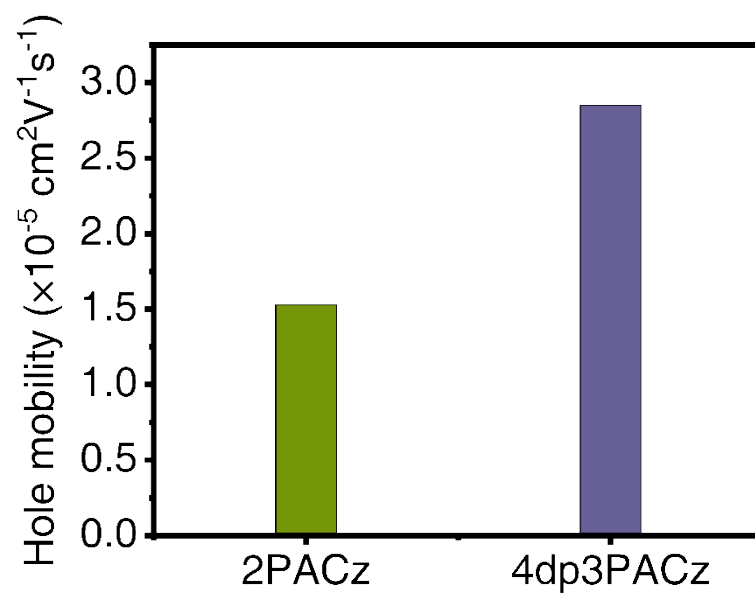


Figure S16. Hole mobility was calculated from the devices with different substrates' SCLC.

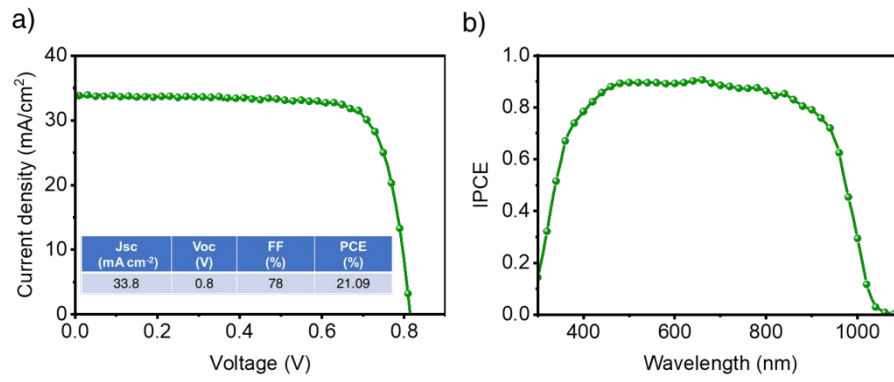


Figure S17. (a)  $J$ - $V$  curve and (b) IPCE curve of the narrow bandgap PSCs used in this work for tandem PSCs.



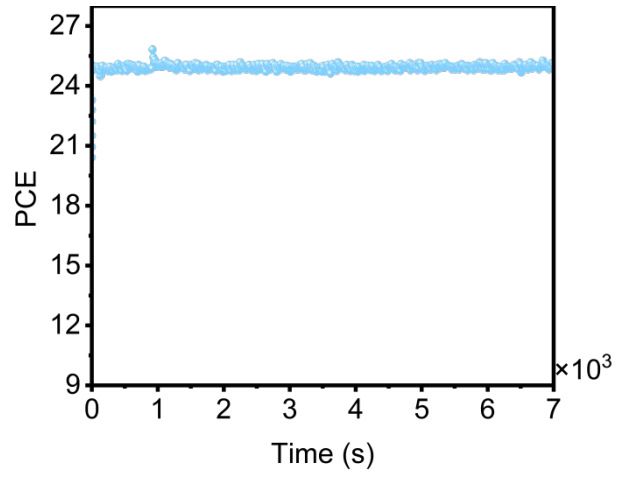


Figure S18. MPPT test of the tandem PSCs with 4dp3PACz as HTL.

Table S1. Series resistance ( $R_s$ ), charge transfer resistance( $R_{ct}$ ) and recombination resistance ( $R_{rec}$ ) of perovskite solar cells with 2PACz or 4dp3PACz as HTL obtained from EIS fitting.

HTL	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_{rec}$ ( $K\Omega$ )
2PACz	195	8.92	31.6
4dp3PACz	157	8.83	41.6

(Device composition: ITO/SAMs/perovskite/GuBr/C60/BCP/Ag, perovskite composition,  $FA_{0.8}Cs_{0.2}PbI_{1.8}Br_{1.2}$ )

Table S2. Fermi level of the different device structure tested by Kelvin probe.

	Fermi level	
	ITO/SAMs (eV)	ITO/SAMs/PVK (eV)
SAMs		
2PACz	5.54	5.59
4dp3PACz	5.60	5.71

Table S3. Summary of champion photovoltaic parameters of devices with PTAA, 2PACz, or 4dp3PACz as HTLs.

HTL	Scan	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF(%)	PCE (%)
PTAA	FS	1.087	15.2	60.85	10.05
	RS	1.022	14.8	59.98	9.07
2PACz	FS	1.132	15.9	64.90	11.68
	RS	1.121	15.4	60.89	10.51
4dp3PACz	FS	1.214	17.8	79.44	17.17
	RS	1.191	17.7	79.01	16.66

(Device composition: ITO/SAMs/perovskite/GuBr/C60/BCP/Ag, perovskite composition, FA<sub>0.8</sub>Cs<sub>0.2</sub>PbI<sub>1.8</sub>Br<sub>1.2</sub>)

Reference:

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