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# **Supporting Information**

## Multifunctional Strategy to Improve Efficiency and Stability of Organic Solar

## Cells via 2PACz/MA Composite Hole Transport Layer

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#### 1. Materials

All materials were purchased from commercial sources. D18, and L8-BO were purchased from Solarmer Materials Inc. DTC11 were purchased from Dongguan Volt-Amp Optoelectronics Technology Co., Ltd. BTP-eC9 was purchased from Nanjing Zhiyan Technology Co., Ltd. 2PACz and myristic acid were purchased from Tokyo Chemical Industry (TCI) Co., Ltd.

### 2. Devices fabrication

The OSC devices were fabricated with conventional structure of ITO/HTL/Active layer/PNDIT-F3N/Ag. The ITO substrates were cleaned by detergent, deionized water and isopropanol under sonication. After being treated with oxygen plasma for about 5 min, 0.27 mg/mL 2PACz was spin-coated on the top of ITO and annealed at 70 °C for 5 min. For the 2PACz HTL, 2PACz solution was used again to rinse the annealed 2PACz film to obtain self-assembled monolayer, which was repeated twice. For the 2PACz/MA composite HTL, the annealed 2PACz film was rinsed once with MA solution (dissolved in o-xylene). MA was spin-coated at different speeds for 30 s in a nitrogen atmosphere without further annealing. All steps were performed in the glove box to ensure consistency. Then, the active layer (D:A=1:1.2, 4 mg mL<sup>-1</sup>:4.8 mg mL<sup>-1</sup>) was dissolved in carbon disulfide and o-xylene (vol.ratio=0.5:0.5) mixed solution, and stirred at 65 °C for 1.5 h in glove box. Later, the active layer with a thickness of approximately 100 nm was spin-coated on the ITO/HTL substrate. Subsequently, PNDIT-F3N solution (1 mg mL<sup>-1</sup> in methanol with 1% acetic acid in volume) was spincoated on the top of the active layer to form a 10 nm cathode interlayer. Finally, a 100 nm Ag layer was deposited by thermal vacuum evaporation under 10<sup>-7</sup> mbar. The effective area of the device was confined to 0.04 cm<sup>2</sup> by a non-refractive mask to improve the accuracy of measurements.

### 3. Characterizations and measurements

**Characterizations:** The atomic force microscopy (AFM) measurements were measured by Digital Instrumental DI Multimode Nanoscope III in a taping mode. UV-vis transmittance spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out using Axis

Supra+ from Kratos Analytical Ltd. CasaXPS software was used for all peak fitting and analysis. Ultraviolet Photoelectron Spectroscopy (UPS) spectra were performed on Thermo Scientific Escalab 250XI apparatus. Scanning Kelvin Probe Microscopy (KPM) were conducted by UHV SKP Measurement (KP Technology Ltd). The grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at Xenocs, France, Xeuss 2.0.

*J-V*, EQE measurements: The current density voltage (*J-V*) characteristics were measured under a computer-controlled Keithley 2400 source meter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The light intensity was calibrated by a standard silicon solar cell (certified by China General Certification Center) before the test, giving a value of 100 mW cm<sup>-2</sup> during the test of *J-V* characteristics. The external quantum efficiency (EQE) spectra were recorded with a QE-R measurement system (Enlitech, QE-R3011, Taiwan).

**Contact angle measurements:** Contact angle measurements were performed using water or ethylene glycol contact angle measurement system (OCA40 Micro). Then the surface free energy was calculated by Owens-Wendt method, as equation S1:<sup>1</sup>

$$\gamma_L \times (1 + \cos\theta) = 2 \times \left(\gamma_L^d \cdot \gamma_{sv}^d\right)^{\frac{1}{2}} + 2 \times \left(\gamma_L^p \cdot \gamma_{sv}^p\right)^{\frac{1}{2}} \#(S1)$$

where  $\gamma_L$  and  $\gamma_{sv}$  are surface free energy of the probe liquid and sample, respectively. The  $\theta$  is the contact angle of the sample. The Flory-Huggins interaction parameter  $\chi_{A-B}$  for blends to show the binary miscibility was calculated from equation S2:

$$\chi_{A-B} = K \left( \gamma_A^{\frac{1}{2}} - \gamma_B^{\frac{1}{2}} \right)^2 \#(S2)$$

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

**Photocurrent density**  $(J_{ph})$  and effective voltage  $(V_{eff})$  measurement:  $J_{ph}$  is calculated as  $J_{ph} = J_L - J_D$ , in which  $J_L$  is the current density under illumination and  $J_D$  is the current density in the dark.  $V_{eff}$  is defined as  $V_{eff} = V_0 - V_{appl}$ , where  $V_0$  is the corresponding voltage when  $J_{ph} = 0$  mA cm<sup>-2</sup>, and  $V_{appl}$  is the applied voltage bias. The

 $G_{\text{max}}$  is defined as  $J_{\text{sat}}/\text{qL}$ , which represents maximum exciton generation rate. P(E, T) is defined as  $J_{\text{ph}}/J_{\text{sat}}$ , which represents exciton dissociation probability.

**Space charge limited current (SCLC) measurement:** The architecture of hole-only device was ITO/HTL/D18/MoO<sub>3</sub>/Ag. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by equation S3.

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}\#(S3)$$

where J is the current density,  $\mu$  is the zero-field mobility,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was calculated by the equation:  $V = V_{appl} - V_{bi} - V_s$ , where  $V_{appl}$  is the applied voltage,  $V_{bi}$  is the built-in voltage, and  $V_s$  is the voltage drop of the substrate series resistance. The hole mobility can be calculated from the slope of the  $J^{1/2}-V$  curves.

**Photo-CELIV measurement:** Photo-CELIV measurement (ramp rate 200 V ms<sup>-1</sup>, delay time: 0 s, offset voltage: 0 V, lightpulse length: 100  $\mu$ s) was performed using allin-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. for different light intensities. The light intensity is given in the maximum power of the LED source (100%  $\approx$  200 mW cm<sup>-2</sup>).

**Transient photocurrent (TPC) and transient photovoltage (TPV) measurements:** The TPC and TPV of the OSCs were measured by applying 500 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short-circuited devices in the dark. The laser pulses were generated from an optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti: sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (Spectra Physics Spitfire Ace). In the transient photoconductivity experiment, the decay of the photocurrent is dominated by carrier sweep out when the bias is 0 and by carrier recombination when the bias is  $V_{\text{OC}}$ . Therefore, the TPC test is shorted at both ends of the device with a small 50  $\Omega$  resistance, as a short circuit of the device, whose purpose is to extract the charge generated in the device. Because the recombination can be almost ignored in short circuit, it is assumed that all the charge is extracted to the outer circuit.<sup>2</sup> The charge

extraction time was extracted from the fitted line of the TPC signal with the equation:  $\delta I = Aexp(t/\tau)$ , where A is a constant that fits the peak height, t is time, and  $\tau$  is the charge extraction time. The transient photovoltage was tested under open circuit conditions to explore the photovoltage decay applied externally to the photodiode with a DC power supply connected in parallel to the oscilloscope. The photovoltage decay kinetics of all devices follow a mono-exponential decay:  $\delta V = Aexp(-t/\tau)$ , where t is the time, and  $\tau$  is the charge carrier lifetime.

**Carrier extraction techniques (CE) and electrochemical impedance spectroscopy (EIS) measurements:** These measurements were performed by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. As for CE measurement, firstly, devices were at open circuit and under light, then the light was turn off, the voltage was set to zero or taken to short-circuit condition within a few hundred nanoseconds to extract charges. The impedance characteristics were measured with the frequency measurement range of 1 Hz to 10 MHz under dark conditions.

**Built-in potential measurement:** The Mott-Schottky measurement was measured by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. It was tested within the voltage range from -3 V to 2 V under dark condition. And the Mott-Schottky equation is described as equation S4.

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \varepsilon_0 \varepsilon_r N} \# (S4)$$

Where *C* is the capacitance value, *V* is the applied voltage, *A* is the device area, *q* is the elementary charge,  $\varepsilon_r$  is the relative dielectric constant,  $\varepsilon_0$  is the vacuum permittivity, and *N* is the charge carrier density.<sup>3</sup>

**EL measurement:** Electroluminescence quantum efficiency (EQE<sub>EL</sub>) was tested by applying external voltage/current sources through the OPV cells (REPS-Pro, Enlitech).

# 4. Supplementary figures and tables



Figure S1. The XPS full spectrum of the corresponding layers on ITO substrate.



Figure S2. Dark current density of common devices based on different HTLs



Figure S3. KPM spectra of ITO, ITO/2PACz and ITO/2PACz/MA.



Figure S4. In situ time-resolved UV-vis absorption spectra of a) 2PACz and b) 2PACz/MA.



**Figure S5.** Transient photovoltage (TPV) and charge extraction (CE) data at open circuit under varying light intensities. a) Carrier Lifetime vary with the voltage. b) Carrier density vary with the voltage. c) Carrier lifetime versus carrier density.



Figure S6. Mott-Schottky curves for devices to obtain  $V_{bi}$ .



Figure S7. Nyquist diagram of the devices measured by electrical impedance spectroscopy (EIS).







**Figure S9.** Images of contact angle measurements of photoactive materials deposited on different HTLs.



**Figure S10.** a) *J-V* curves and b) EQE spectra of D18:L8-BO blends based on different HTLs



Figure S11. a) *J-V* curves and b) EQE spectra of D18:BTP-eC9 blends based on different HTLs



**Figure S12.** a) *J-V* curves and b) EQE spectra of D18:L8-BO:BTP-eC9 blends based on different HTLs

E:1m	Contact	Contact angle (°)			
F IIIII	$H_2O$	EG	$\gamma_{\rm s}$ (min m <sup>-1</sup> )	$\chi_{\rm HTL/D18}(k)$	
2PACz	80.88	45.34	39.74	2.21	
2PACz/MA	82.66	51.21	35.11	1.23	
D18	103.56	77.85	23.20	/	

**Table S1.** Summary of contact angle results about HTLs.

Table S2. Detailed results extracted from the UPS measurements.<sup>a)</sup>

HTL	$E_{\text{cut-off}}(eV)$	WF (eV)
2PACz	16.37	4.85
2PACz/MA	16.14	5.08

<sup>a)</sup> UPS test results have been calibrated with Ag standard samples.

Table S3.	Work function	(WF) measured	by scanning	Kelvin probe	microscopy.

	ITO	2PACz	2PACz/MA
WF (eV)	4.70	4.89	4.90

Concentration (mg mL <sup>-1</sup> )	V <sub>OC</sub> (V)	$J_{ m SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0	0.874	27.98	78.91	19.30
0	$0.874 {\pm} 0.001$	27.91±0.09	$78.48 \pm 0.60$	19.14±0.23
0.2	0.872	28.43	79.44	19.69
0.3	$0.874 {\pm} 0.004$	27.95±0.68	80.19±1.05	19.59±0.14
0.4	0.871	28.60	79.42	19.79
0.4	$0.873 {\pm} 0.001$	28.36±0.23	79.38±0.11	19.64±0.16
0.5	0.879	28.32	80.10	19.93
0.5	$0.876 \pm 0.003$	28.27±0.11	$80.09 \pm 0.62$	19.82±0.20
0.6	0.875	28.07	80.20	19.71
0.6	$0.875 {\pm} 0.000$	28.15±0.12	79.90±0.42	19.69±0.02
0.7	0.875	28.18	79.31	19.56
	$0.876 \pm 0.000$	28.05±0.18	79.42±0.15	19.51±0.08
1.0	0.868	28.11	79.87	19.49
1.0	0.867±0.001	27.99±0.17	79.77±0.14	19.36±0.18

**Table S4.** Detailed photovoltaic parameters of devices based on differentconcentrations of MA that spin-coating on 2PACz.

**Table S5.** Detailed photovoltaic parameters of devices based on different spin-coating speed of 0.5 mg mL<sup>-1</sup> MA.

Speed (rpm)	V <sub>oc</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
2000	0.871	28.20	79.71	19.58
	$0.8/1\pm0.000$ 0.877	28.14±0.08 28.05	79.46±0.35 80.70	19.48±0.14 19.86
4000	0.877±0.001	28.01±0.05	79.93±1.08	19.63±0.32
6000	0.879	28.32	80.10	19.93
6000	$0.876 \pm 0.003$	28.27±0.11	80.09±0.62	19.82±0.20
8000	0.875	28.13	79.87	19.67
8000	$0.876 {\pm} 0.003$	27.95±0.30	80.09±0.33	$19.60 \pm 0.08$

**Table S6.** Detailed photovoltaic parameters of the devices prepared based on the modified layers with different alkyl chain lengths spin-coated on 2PACz. Specifically, C12A represents dodecanoic acid, C14A represents tetradecanoic acid, which is the MA reported in this work, and C16A represents hexadecanoic acid. The active layer is D18:DTC11.

NA 1°C 11	$V_{\rm OC}$	$J_{ m SC}$	FF	PCE
Modified layer	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
,	0.874	27.98	78.91	19.30
W/O	$0.874 \pm 0.001$	27.91±0.09	78.48±0.60	19.14±0.23
C12A	0.875	28.13	79.87	19.67
	$0.876 \pm 0.002$	28.09±0.17	79.81±0.68	19.63±0.04
	0.879	28.32	80.10	19.93
C14A (MA)	0.876±0.003	28.27±0.11	80.09±0.62	19.82±0.20
01()	0.875	27.79	80.51	19.57
C16A	0.876±0.003	27.76±0.14	80.32±0.29	19.53±0.04

**Table S7.** Detailed calculated results from  $J_{\rm ph}$  -  $V_{\rm eff}$  measurement.

HTL	$J_{\rm ph \ (V = 0)}$ (mA cm <sup>-2</sup> )	$J_{\rm sat}$ (mA cm <sup>-2</sup> )	G <sub>max</sub> (m <sup>-3</sup> s <sup>-1</sup> )	<i>P</i> (E, T) (%)
2PACz	27.41	27.86	1.74×10 <sup>28</sup>	98.38
2PACz/MA	28.10	28.23	$1.76 \times 10^{28}$	99.54

Table S8. Detailed carrier mobility results from Photo-CELIV measurement.

	2PACz	2PACz/MA
μ (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )	2.06×10 <sup>-4</sup>	2.43×10 <sup>-4</sup>

HTL	$R_{\rm s}(\Omega)$	$R_{ m bulk}$ (k $\Omega$ )	$C_{\text{bulk}}$ (nF)	$R_{ m interface}\left(\Omega ight)$	$C_{\text{interface}}(\mathrm{nF})$
2PACz	20.9	2.39	4.1	20.3	10.0
2PACz/MA	11.1	0.37	10.4	10.8	3000.0

**Table S9.** Summary of impedance data obtained from circuit simulation in Nyquist diagram.

 Table S10. Detailed results of voltage loss measurements.

HTL	$E_{g}/q$ (V)	$\Delta V_{\rm OC}^{\rm rad}({ m V})$	$\Delta V^{\rm rad, \ below \ gap}_{\rm OC} (V)$	$\Delta V_{OC}^{\text{non - rad}}(V)$
2PACz	1.414	0.262	0.062	0.214
2PACz/MA	1.414	0.262	0.061	0.207

**Table S11.** Summary of contact angle results of photoactive materials deposited on different HTLs.

HTL	Film	Contact angle (°)			
	ГШП —	H <sub>2</sub> O	EG	$\gamma_{\rm s}$ (IIIIN III -)	χD18:DTC11 ( <b>K</b> )
2PACz	D18	105.22	79.75	22.46	/
	DTC11	104.72	75.93	27.46	0.25
	D18	103.81	77.81	23.54	/
2PACz/MA	DTC11	105.74	77.12	26.99	0.12

HTL	Peak	Peak	$\pi$ - $\pi$ stacking	EW/LIM	Crystal
		location	distance	$\Gamma$ W $\Pi$ W	coherence
		(Å-1)	(Å)	$(\mathbf{A}^{\mathbf{r}})$	length (Å)
2PACz	(100) In IP	0.298	/	0.072	88.3
	(010) In OOP	1.741	3.61	0.256	24.5
2PACz/MA	(100) In IP	0.298	/	0.070	90.1
	(010) In OOP	1.741	3.61	0.257	24.5

Table S12. Summary of GIWAXS results.

**Table S13.** Summary of photovoltaic parameters obtained by applying different HTLs

 in the three most common active layer systems.

Active layer	HTL	$V_{\rm OC}$	$J_{ m SC}$	$J_{cal}$	FF	PCE
		(V)	(mA/cm <sup>2</sup> )	(mA/cm <sup>2</sup> )	(%)	(%)
D18:L8-BO	2PACz	0.883	27.07	25 60	79.83	19.09
		0.886±0.003	26.95±0.18	23.09	79.66±0.24	19.01±0.11
	2PACz/M	0.897	27.05	06.05	81.14	19.68
	А	0.895±0.002	27.08±0.05	26.05	81.04±0.14	19.65±0.05
D18:BTP- eC9	2PACz	0.858	28.16	27.22	79.21	19.14
		0.860±0.003	28.15±0.11	21.23	78.73±0.36	19.05±0.08
	2PACz/M	0.862	28.80	28.07	79.91	19.83
	А	0.860±0.003 28.77±0.05		28.07	79.82±0.13	19.74±0.13
D18:L8- BO:BTP- eC9	2PACz	0.880	28.07	26.71	78.63	19.42
		0.882±0.002 27.70±0.27		20.71	78.93±0.54	19.29±0.11
	2PACz/M	0.886	28.40	27.00	79.58	20.02
	А	0.886±0.001	).886±0.001 28.21±0.22		79.83±0.49	19.96±0.05

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