Supplemental Information

Blade-Coated Organic Photovoltaics with Dichlorophthalic Acid Self-Assembled Monolayer

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Supplemental Experimental Procedures

1. Materials

PEDOT: PSS (Al4083) was purchased from Heraeus Clevis. PM6, BO-4Cl, Y6, BTP-eC9 and PDINN were purchased from Solarmer Materials (Beijing) Inc and Hyper Inc. and were used without any further purification. Chlorobenzene was purchased from J&K Scientific, Inc. Other chemicals were purchased from Titan Technology (Shanghai), Inc.

2. OPV devices fabrication

OPV devices were fabricated in device configuration of ITO/PEDOT:PSS/active layers/PDINN/Ag and ITO/active layers: 2C2BA/PDINN/Ag.

The ITO substrates were first cleaned by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 20 min before use. PEDOT:PSS (Al4083) was spincast onto the ITO substrates at 3000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The 2C2BA was dissolved in isopropanol (2 mg mL^{-1}). 5% volume ratio 2 mg mL^{-1} of 2C2BA needs to be added to the active layer solution. The 2C2BA SAM self-assembles after co-mixing with the donor:acceptor solution, obviating extra monolayer processing. The PM6:BO-4Cl blend (1:1.2 weight ratio) was dissolved in chlorobenzene with 0.15% volume ratio DIO (the PM6 concentration was 7 mg mL^{-1}), and stirred for 1 h on a hotplate at 80 °C in a nitrogen-filled glove box. The PM6:BO-4Cl blend solution was blade-coated at a 40 °C hotplate at different coating speed, and then transferred to a nearby hotplate to be annealed at a 100 °C hotplate for 5 min. The gap between silicon blade and substrate is 150 μm. No nitrogen knife was installed to assist the film forming process. The thickness of the active layer is around 100 nm.

For 2 cm^2 area devices, the blade coated films were fabricated by chlorobenzene with 0.1% volume ratio DIO solutions (7 mg mL^{-1} donor concentration, 80 °C stirred for 1h.) with a 20 mm s-1 speed forward and backward (the blade-substrate gap is 100 μm) on 60 °C substrates, and then transferred to a nearby hotplate to be annealed at a 100 °C hotplate for 5 min. No Nitrogen knife was installed to assist the film forming process as well.

A thin PDINN layer was coated on the active layer, followed by the deposition of 100nm Ag (evaporated under 5×10^{-5} Pa through a shadow mask). The current density-voltage (*J*-*V*) curves of devices were measured using a Keysight B2901B Source Meter in glove box under AM 1.5G (100 mW cm^{-2}) using a Enlitech solar simulator. The device area was 0.039 cm^2 for small area devices and 2 cm^2 for large area devices. The voltage range is -0.5 V to 1.2 V. The step is 0.02 V with delay time of 10 ms. The device is tested in glovebox filled with N2, at room temperature. A 2×2 cm^2 monocrystalline silicon reference cell with KG5 filter (purchased from Enli Tech. Co., Ltd.). The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R (Enlitech Co.Ltd.). The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell.

3. UV-vis absorbance and transmittance measurements

The UV-vis spectrophotometer (UV-2600i, Shimadzu Instruments (Suzhou), Inc.) was used for UV-vis absorbance and transmittance measurements. The preparation process of PEDOT: PSS and 2C2BA is completely consistent with that used in the device.

4. XPS measurements

Instrument model: AXIS Supra (Kratos). The power of survey scan: 15 kV, 5 mA; The power of region scan: 15 kV, 5mA. XPS defaults to using C 1s (284.6 eV) calibration for all spectra.

5. Contact angle measurements

The optical contact angle measuring instrument was used to measure the contact angle, and water and diiodomethane were selected as the liquid phase. The values of diiodomethane contact angle and water contact angle are used to calculate the surface free energy. The surface free energy models used here are Owens, Wendt, Rabel and Kaelble (OWRK).

6. AFM measurements

AFM measurements were performed by using Dimension Icon atomic force microscopy (Bruker) using the tapping mode.

7. GIWAXS measurements

GIWAXS data were obtained at beamline BL02U2 of Shanghai Synchrotron Radiation Facility (SSRF). The monochromatic of the light source was 1.24 Å. The data were recorded by using the two-dimensional image plate detector of Pilatus 2M from Dectris, Switzerland.

8. TPC and TPV measurements

The transient photovoltage (TPV) measurement was conducted under 1 sun illumination with a white light-emitting diode, and the device was set to the open-circuit condition. While the device was set to the short-circuit condition in the dark for the transient photocurrent (TPC) measurement. The output signal was collected by keysight oscilloscope for both TPV and TPC.

9. KPFM measurements

Model of the equipment: ICON atomic force microscope, Bruker, Germany. Model of the probe: MESPA-V2. Scanning range: 5 μm ×5 μm.

Supplemental Figures and Tables

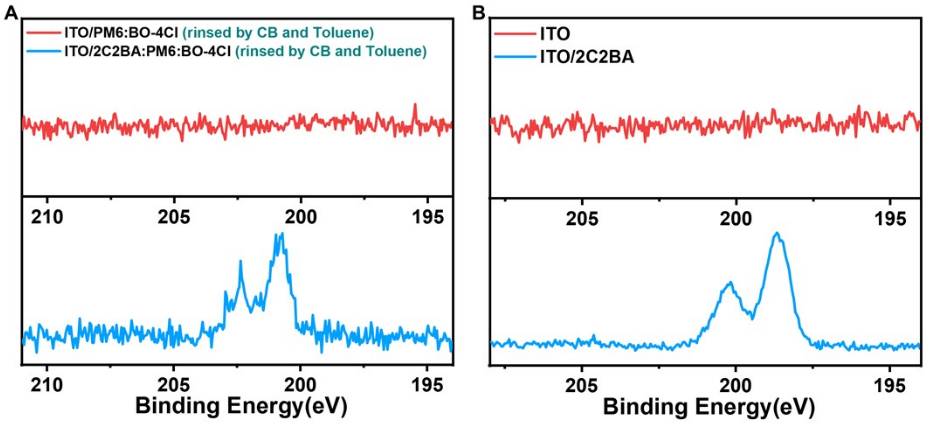

Figure S1. XPS Cl 2p spectra of (A) ITO/PM6:BO-4Cl and ITO/2C2BA:PM6:BO-4Cl. Each sample was rinsed by CB and toluene for 8 times and (b) ITO and ITO/2C2BA.

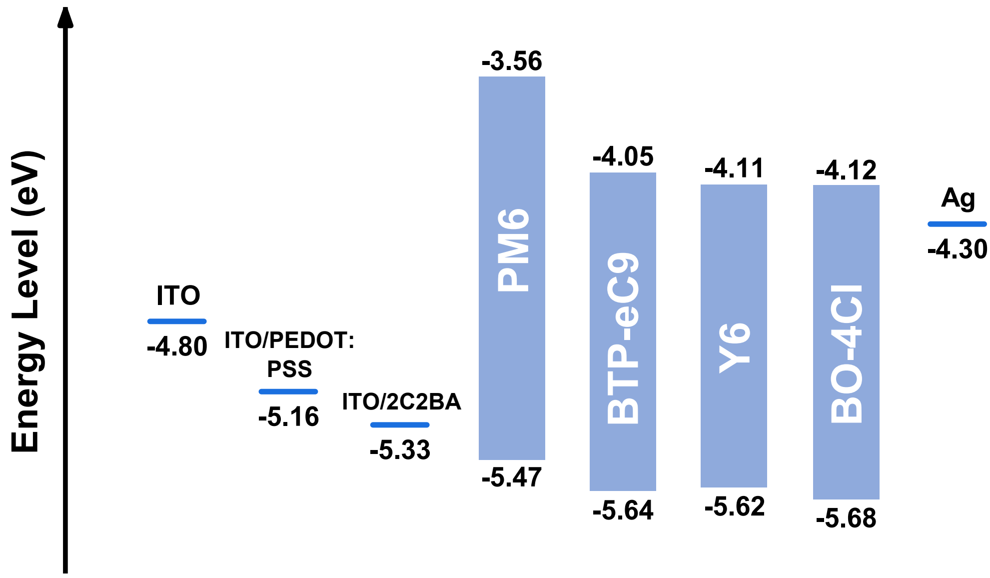

Figure S2. Energy Level diagram of ITO, ITO/PEDOT:PSS, ITO/2C2BA, PM6, BTP-eC9, Y6, BO-4Cl, and Ag.

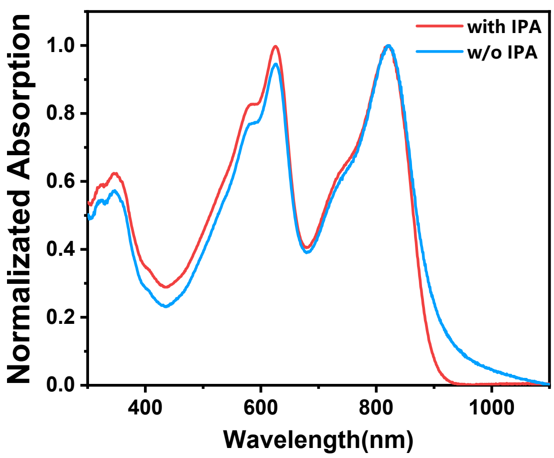

Figure S3. Normalized absorption spectra of PM6:BO-4Cl blend films cast from active layer CB solution and active layer CB:IPA mixed solution.

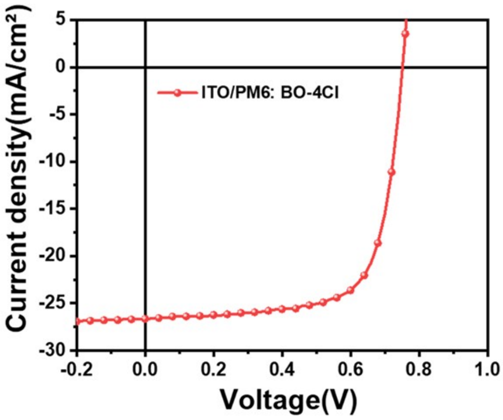

Figure S4. The *J-V* curve of device without anode interfacial layer under illumination of AM 1.5G (100 mW cm^{-2}).

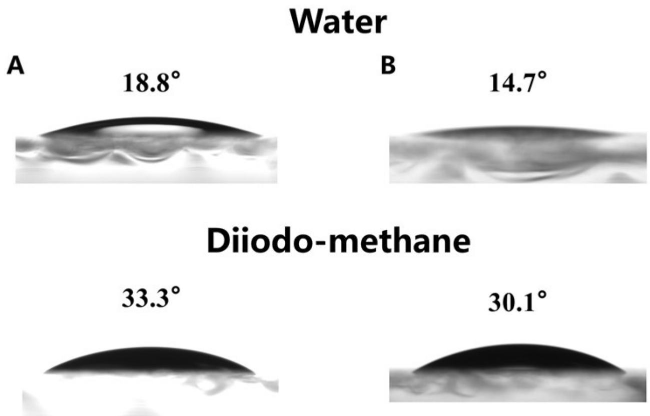

Figure S5. Optical contact angle of (A) ITO and (B) PEDOT:PSS.

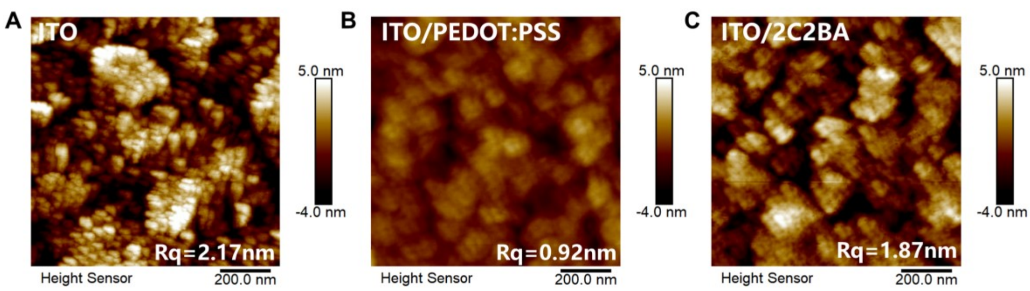

Figure S6. AFM images and surface roughness of (A) ITO, (B) ITO/PEDOT:PSS and (C) ITO/2C2BA.

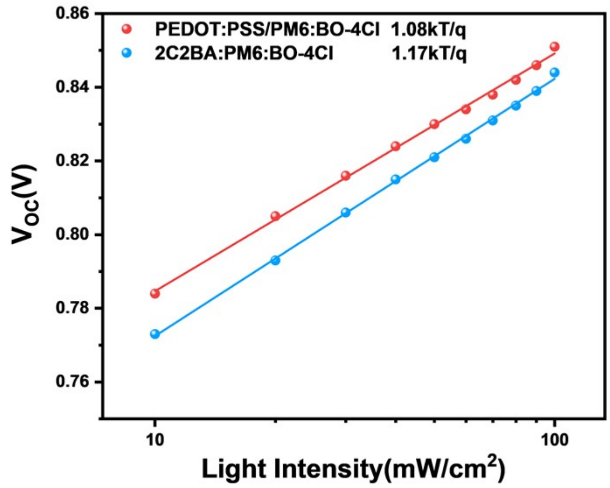

Figure S7. V_{OC} versus light intensity characteristics.

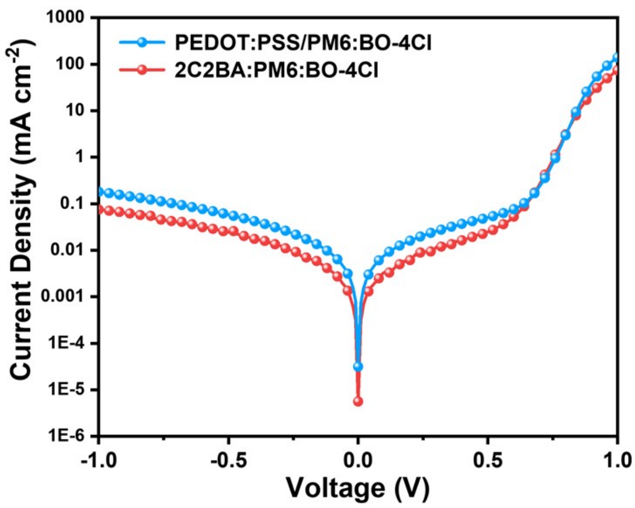

Figure S8. Dark current density of OPV devices based on different AILs.

Table S1. Photovoltaic parameters of AIL-free OPV devices.

Device structure	V_{OC} (V) [a]	J_{SC} [a] (mA cm^{-2})	FF (%) [a]	PCE (%)		Area
				Average [a]	Best	(cm^2)
ITO/PM6:BO-4Cl	0.761±0.009	25.97±0.6	69.7±1.8	13.8±0.4	14.2	0.039

[a] Average value obtained from eight independent devices.

Table S2. The photovoltaic parameters based on different device structures.

Device structure	V_{OC} (V) [a]	J_{SC} [a] (mA cm^{-2})	FF (%) [a]	PCE (%)	
				Average [a]	Best
ITO/2C2BA/PM6:BTP-eC9/PDINN/Ag	0.853±0.004	27.8±0.3	73.6±0.5	17.5±0.2	17.8
ITO/2C2BA:PM6:BTP-eC9/PDINN/Ag	0.848±0.003	28.1±0.3	73.3±0.6	17.5±0.2	17.8

[a] Average value obtained from eight independent devices.

Table S3. Wettability and surface energy characteristics of diverse material films.

Material	Water contact angle	Diiodomethane contact angle	Surface energy (mN m^{-1})
PM6	105.6°	57.7°	30.0
BO-4Cl	95.1°	32.9°	43.1
2C2BA	73.7°	36.5°	46.8
PEDOT:PSS	14.7°	30.1°	76.5
ITO	18.8°	33.3°	74.7

Table S4. The detail parameters of PM6:BO-4Cl film and 2C2BA:PM6:BO-4Cl film of (100) peak and (010) peak.

Film	Peak	q ($Å^{-1}$)	d-space (Å) [a]	FWHM ($Å^{-1}$)	CCL(Å) [b]
PM6:BO-4Cl	(100)	0.29	21.48	0.19	30.2
	(010)	1.74	3.61	0.24	23.6
2C2BA:PM6:BO-4Cl	(100)	0.30	21.30	0.18	31.1
	(010)	1.77	3.55	0.22	25.5

[a] d-space: d= 2π/q, [b] CCL= 2πk/q, k=0.89

Table S5. Parameters of OPV devices based on PM6:BO-4Cl with PEDOT:PSS and 2C2BA.

AIL	V_0 (V)	J_{SC} (mA cm^{-2})	J_{sat} (mA cm^{-2})	P_{diss} (%)	P_{coll} (%)
PEDOT: PSS	0.860	25.3	26.4	95.9	85.3
2C2BA	0.841	26.4	27.2	97.1	87.1

Table S6. Photovoltaic parameters of OPV devices based on the PM6:Y6 system.

AIL	V_{OC} (V) [a]	J_{SC} [a] (mA cm^{-2})	*calc.* J_{SC} [b] (mA cm^{-2})	FF (%) [a]	PCE (%)		Area (cm^2)
					Average [a]	Best	
PEDOT: PSS	0.826±0.004	27.0±0.2	25.8	73.4±0.6	16.3±0.2	16.5	0.039
2C2BA	0.830±0.003	27.3±0.1	26.2	73.3±1.1	16.6±0.2	16.9	

[a] Average value obtained from eight independent devices; [b] Calculated by integrating the EQE spectrum.

Table S7. Performance of OPV device or modules (area ≥ 1 cm^2) with self-assembly monolayer layer.

Device structure	Device area (cm^2)	Year	PCE (%)	Ref.
ITO/DPO:PM6:BTP-eC9/MoO_3/Ag	0.98	2022	13.2	[1]
ITO/2PACz:PM6:Y6-BO/PNDIT-F3N/Ag	1	2022	15.8	[2]
ITO/PEDOT:PSS/2PACz/PM6:BTP-eC9/PNDIT-F3N-Br/Ag	1	2023	13.3	[3]
ITO/BnPA/F5BnPA/PM6:BO-4Cl/PFN-Br/Ag	1.05	2023	15.3	[4]
ITO/4PDACB/D18: L8-BO/PNDIT-F3N/Ag	19.3	2024	15.44	[5]
ITO/PTA/PM6:Y6:$PC_{71}BM$/PFN-Br/Ag	54	2024	15.18	[6]
ITO/PTA:PM6:Y6:$PC_{71}BM$/PFN-Br/Ag	54	2024	13.90	[6]
ITO/Br-PA:HPWO/PM6:BTP-eC9:L8-F/PDINOH/Ag	1	2024	17.23	[7]
ITO/2PACz-SAI/PM6:BTP-eC9:L8-BO/PDINN/Ag	1.05	2024	18.41	[8]
ITO/2C2BA:PM6:BO-4Cl/PDINN/Ag	2	2024	16.69	This work

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