Supporting Information

Self-Assembled Monolayer as a Hole-Transport Layer Forming a Robust Interface with the Active Layer for Enhanced Thermal Stability in Organic Solar Cells

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Experimental

1. Materials.

The Heraeus PEDOT:PSS AI4084, PM6, Y6, and MeO-2PACz were purchased from omniscience, 1-Materials, GR-Chem, and Lumtec., respectively.

2. Device fabrication.

ITO washed in the following order of DI water, ethanol, acetone, and isopropyl alcohol for each 15 min. Before deposit PEDOT:PSS, 15 min UV/O treatment was conducted for increasing surface energy with hydrophilic -OH groups. Onto the ITO, PEDOT:PSS AI4084 is formed by spin-coating process of 4000 rpm, 30 sec. The remaining water is evaporated after 15 min heating at 150°C. In the case of MeO-2PACz, 1 mM MeO-2PACz was dissolved in anhydrous isopropyl alcohol and stirred overnight. MeO-2PACz solution was spin coated with the condition of 3000 rpm 30sec in glove box after 30 min UV/O treatment. 6.3 mg PM6 and 7.7 mg Y6 was dissolved in chloroform and stirred for 4 hr. Under N2 condition, the photoactive solution spin coated onto the HTMs, then annealed at 110°C for 10 min. Afterward, PFN-Br solution (0.5wt% in methanol) was deposited onto photoactive layer. Aluminium was thermally evaporated to a thickness of 100 nm below 1.0 · 10-6 torr. The encapsulation was conducted in glove box to prevent the oxidation.

3. UV-VIS measurement

The bare films on ITO of PEDOT:PSS, MeO-2PACz, and PM6:Y6 were identical with device fabrication casting method. Wavelength range is from 300 nm to 1100 nm.

4. RAMAN measurement.

The RAMAN intensity was obtained when proved at 532 nm. Imaging scanning size is 15 μm by 15 μm . The conditions of spectral center, integrating time and accumulation are 1800 nm, 0.05 and 10, respectively.

5. (In-situ) GIWAXS measurement.

All films were spin-coated on a Si substrate from chloroform solutions (14 mg/ml) at 3000 rpm for 30 sec. The ratio of donor (PM6) and acceptor (Y6) was 1:1.2. The concentration for bare films of PM6 and Y6 are both 10 mg/ml in chloroform. GIWAXS experiment was conducted with a sample-to-detector distance of 212 mm, an X-ray radiation beam energy of 10.26 keV, and an incidence angle of 0.13°. All films were analyzed in a vacuum chamber.

6. Depth profile XPS measurement.

The depth profile XPS was sputter for 50 times with 0.40 min interval. The depth energy is 3kV for 2 mm·2 mm area samples. Each film was ITO/PEDOT:PSS/PM6:Y6 and ITO/MeO-2PACz/PM6:Y6 before and after 65°C for 12 hr aging. Film casting condition is same as device fabrication method.

7. EIS measurement.

In order to focus on the interface condition between HTM and photoactive layer, a device with electron transporting layer removed was fabricated. The device structures are ITO/PEDOT:PSS/PM6:Y6/Ag and ITO/MeO-2PACz/PM6:Y6/Ag. To minimize the degradation through the electrode, silver was selected instead of the aluminum. Frequency range was from 7 MHz to 10 Hz with applying open circuit voltage under 1 SUN illumination.

8. TPC measurement.

For the same cause as the EIS measurement, the device structure was fabricated as follows. ITO/PEDOT:PSS/PM6:Y6/Ag and ITO/MeO-2PACz/PM6:Y6/Ag. Pulsed light was applied at 20 mA under dark.

9. TRPL measurement.

The precursor of PM6 solution in chloroform was prepared with 10 mg/ml concentration. The 10 mg/ml solution stirred at room temperature for 3 hr, and then diluted to concentration of 0.25, 0.5, 1, 2.5, and 5 mg/ml, respectively. The sample was spin coated on UV/O treated glass with the spin-coating method. In glove box, spin coating was conducted at 3000rpm for 30sec. The excitation was 697 nm, where the photoluminescence peak of PM6 showed maximum.

10. SCLC measurement.

Each device was fabricated with spin-coating method in glove box. The PEDOT:PSS was deposited on 15 min UV/O treated glass with the condition of 4000 rpm, 30sce and 150°C, 15min annealing in air. In MeO-2PACz samples, the film was spin coated on 30 min UV/O treated for 3000rpm, 30s, and annealing process at 100°C was performed for 10 min. To remove unreacted residue, we performed washing process with IPA solvent in glove box. Subsequently, the optimized 0.5 mg/ml PM6 was spread on each hole transporting materials. Silver was thermally deposited 80nm under a vacuum below $1.0 \cdot 10^{-6}$ torr.

Note, Figure and Table legends

Note S1. Considerations on TPC Decay Shape and Extraction Time Evaluation.

Figure S1. Chemical structure of Y6, PM6, PEDOT:PSS and MeO-2PACz.
Figure S2. (a) Diagram of the adhesion-test method. (b) Film photographs for PEDOT:PSS/PM6:Y6 and MeO-2PACz/PM6:Y6 before and after the adhesion test.
Figure S3. *In-situ* Grazing-incidence wide-angle X-ray scattering (GIWAXS) of (a) PM6 and (b) Y6.
Figure S4. **.** Ultraviolet-visible spectroscopy results before and after the peeling test of (a) PEDOT:PSS/PM6:Y6 and (b) MeO-2PACz/PM6:Y6 films.
Figure S5. (a) Pristine Raman results of Y6, PM6, PEDOT:PSS, the SAM, and ITO substrate. Here, H and P represent the peak points of PEDOT:PSS and PM6:Y6, respectively, and are indicated in purple and blue in the Raman image. Remaining or bare films of (b) PEDOT:PSS/PM6:Y6 and (c) MeO-2PACz/PM6:Y6 before and after the adhesive test. Line-scan Raman image of a combination of H and P marked in Figure 2a
Figure S6. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping results of (a) pristine ITO/2MeO-2PACz, (b) pristine ITO/MeO-2PACz/PM6:Y6, (c) remained ITO/MeO-2PACz/PM6:Y6 film after peeling test, and (d) 65°C aged ITO/MeO-2PACz/PM6:Y6 film after peeling test. The analysed elements, from left to right, are indium (In), phosphorus (P), carbon (C) and sulphur (S).
Figure S7. Depth profile XPS raw data of (a) pristine ITO/PEDOT:PSS/PM6:Y6 film, (b) aged ITO/PEDOT:PSS/PM6:Y6 film at 65°C for 12 h, (c) pristine ITO/MeO-2PACz/PM6:Y6 film and (d) aged ITO/MeO-2PACz/PM6:Y6 film at 65°C for 12 h.
Figure S8. Time-resolved photoluminescence (TRPL) graph and T_{80} lifetime depending on PM6 concentration of 0.25, 0.5, 1, 2.5, 5 and 10 mg/ml in chloroform. The optimal concentration condition is 0.5 mg/ml.
Figure S9. Space charge limited current (SCLC) plots of (a) 0.5 mg/ml PM6 over aging time at 65°C. SCLC plots of (b) as-cast and annealed PEDOT:PSS/PM6 and (c) as-cast and annealed MeO-2PACz/PM6 at 65°C for 12 h.
Figure S10. Time-dependent J–V curves of a representative device from the stability tests of ITO/HTL/PM6:Y6/PFN-Br/Ag structures using (a) PEDOT:PSS and (b) MeO-2PACz as the HTL.

Table S1. Contact angle of water and glycol and calculated surface energy from average contact angle values.
Table S2. Device efficiencies depending on HTL of 10 different devices with device structures of ITO/HTL/PM6:Y6/PFN-Br/Ag.
Table S3. Raw data of PCE stability vs. annealing time for TO/HTL/PM6:Y6/PFN-Br/Ag devices using PEDOT:PSS or MeO-2PACz as HTL.

Video S1. Universal peeling test for pristine PEDOT:PSS/PM6:Y6 film..

Video S2. Universal peeling test for aged PEDOT:PSS/PM6:Y6 film.

Video S3. Universal peeling test for pristine MeO-2PACz/PM6:Y6 film after 40 min resting time.

Video S4. Universal peeling test for aged MeO-2PACz/PM6:Y6 film after 40 min resting time.

Note S1. Considerations on TPC Decay Shape and Extraction Time Evaluation.

The transient photocurrent (TPC) responses observed in this study do not strictly follow mono-exponential decay, due to overlapping processes such as interface-limited extraction, trap-mediated recombination, and field-assisted carrier transport. Thus, the extraction time values extracted from fitting are intended as comparative indicators between device configurations rather than absolute time constants.

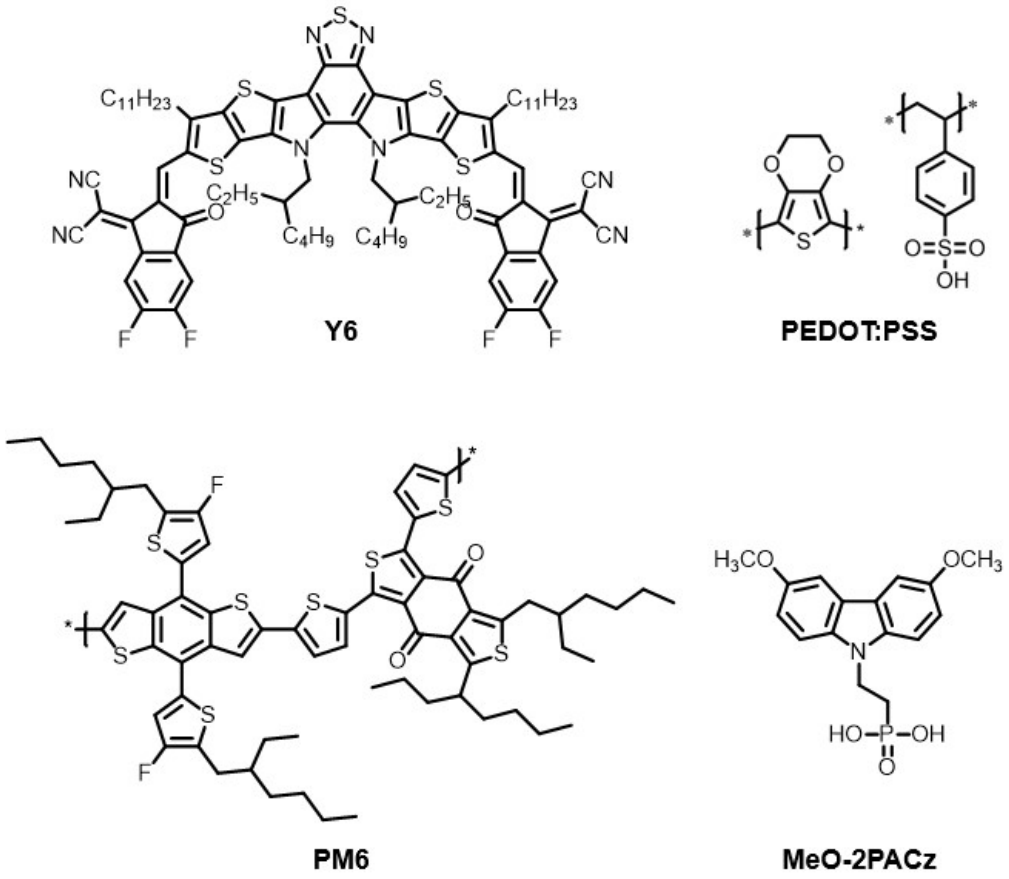

Figure S1. Chemical structures of Y6, PM6, PEDOT:PSS and MeO-2PACz.

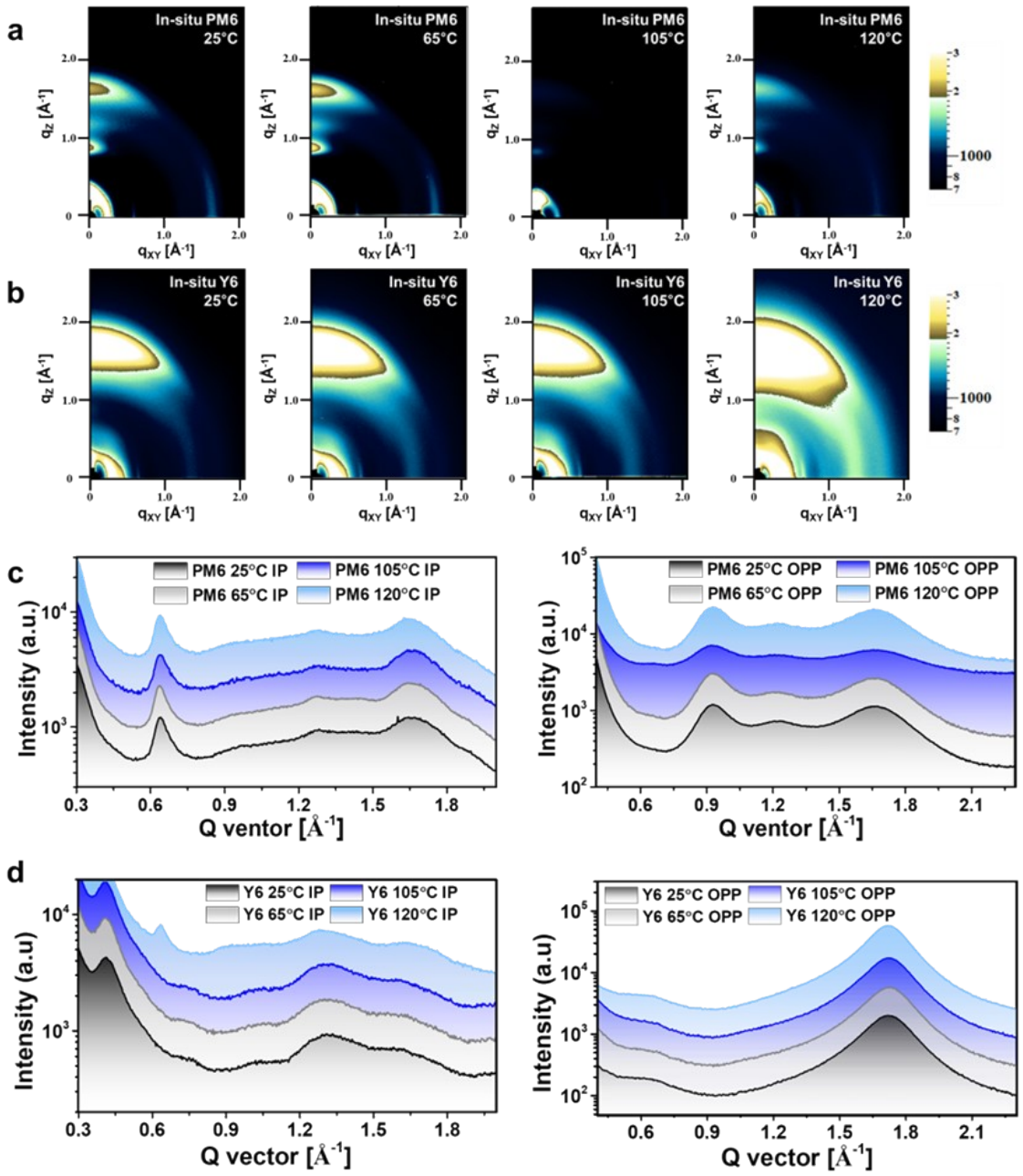

Figure S2. *In-situ* GIWAXS of (a) PM6 and (b) Y6. The (c) *in-plane* and (d) *out-of-plane* line-cut profiles of PM6 and Y6 extraced from the 2D GIWAXS patterns. The abbreviations IP and OPP denote *in-plane* and *out-of-plane*, respectively.

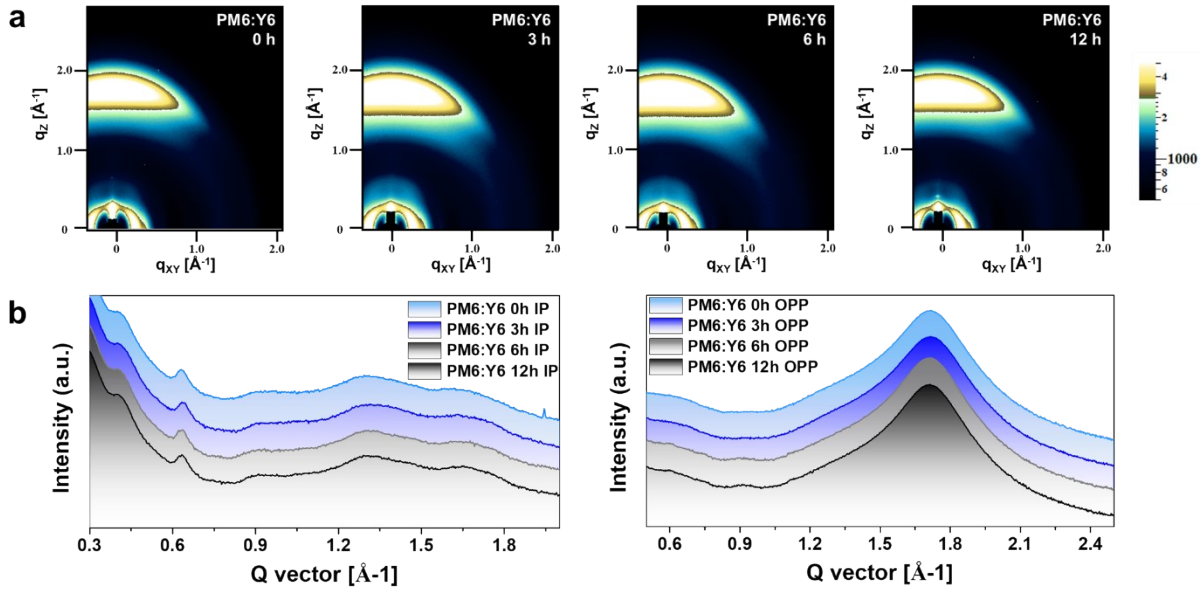

Figure S3. (a) GIWAXS diffraction patterns and (b) GIWAXS linecut profiles of PM6:Y6 film over time at 65°C. The abbreviations IP and OPP denote *in-plane* and *out-of-plane*, respectively.

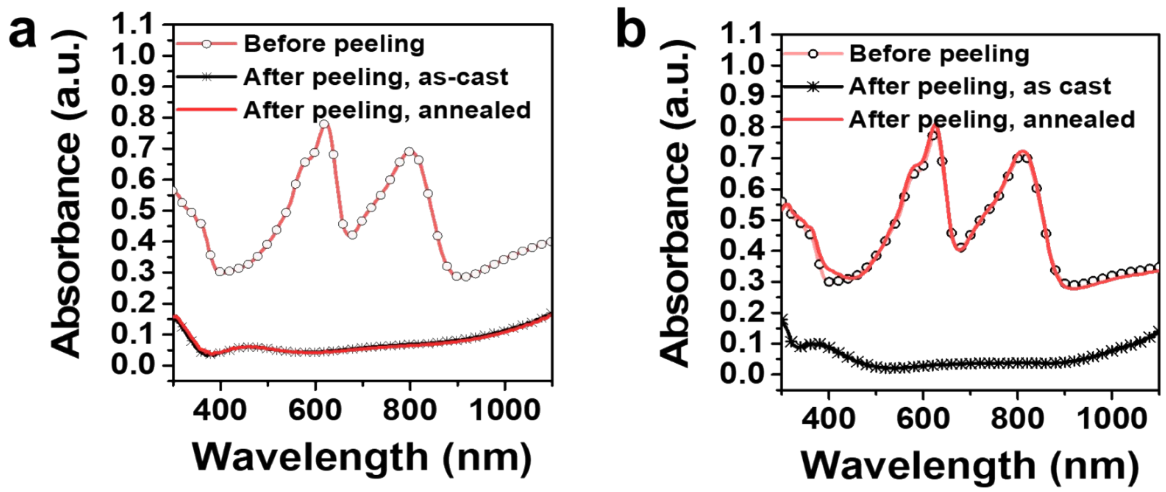

Figure S4. UV-vis absorption spectra before and after the peeling test of (a) PEDOT:PSS/PM6:Y6 and (b) MeO-2PACz/PM6:Y6 films.

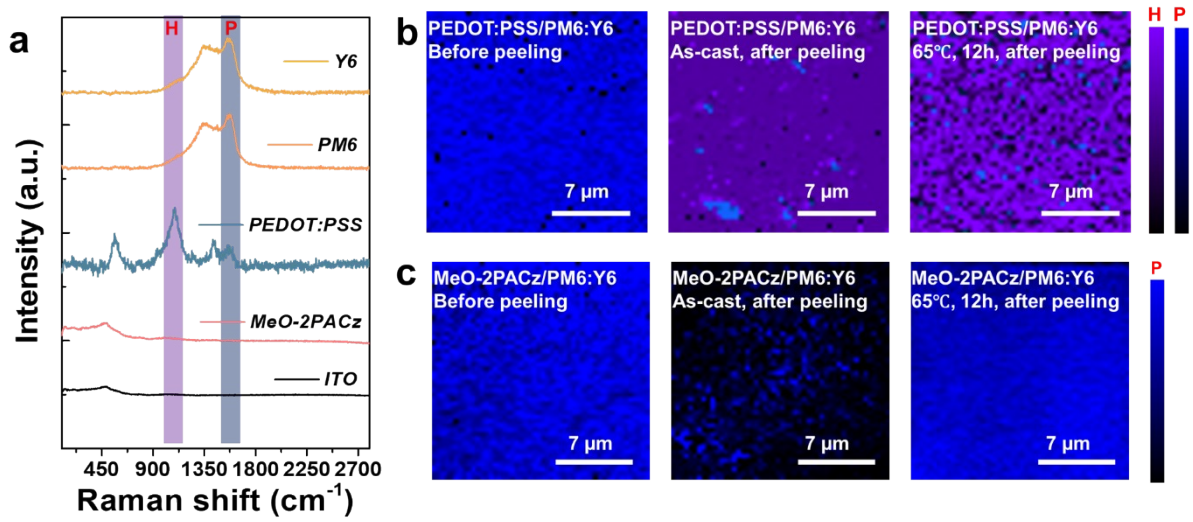

Figure S5. (a) Pristine Raman results of Y6, PM6, PEDOT:PSS, the SAM, and ITO substrate. Here, H and P represent the peak points of PEDOT:PSS and PM6:Y6, respectively, and are indicated in purple and blue in the Raman image. The films of (b) PEDOT:PSS/PM6:Y6 and (c) MeO-2PACz/PM6:Y6 before and after the peeling test.

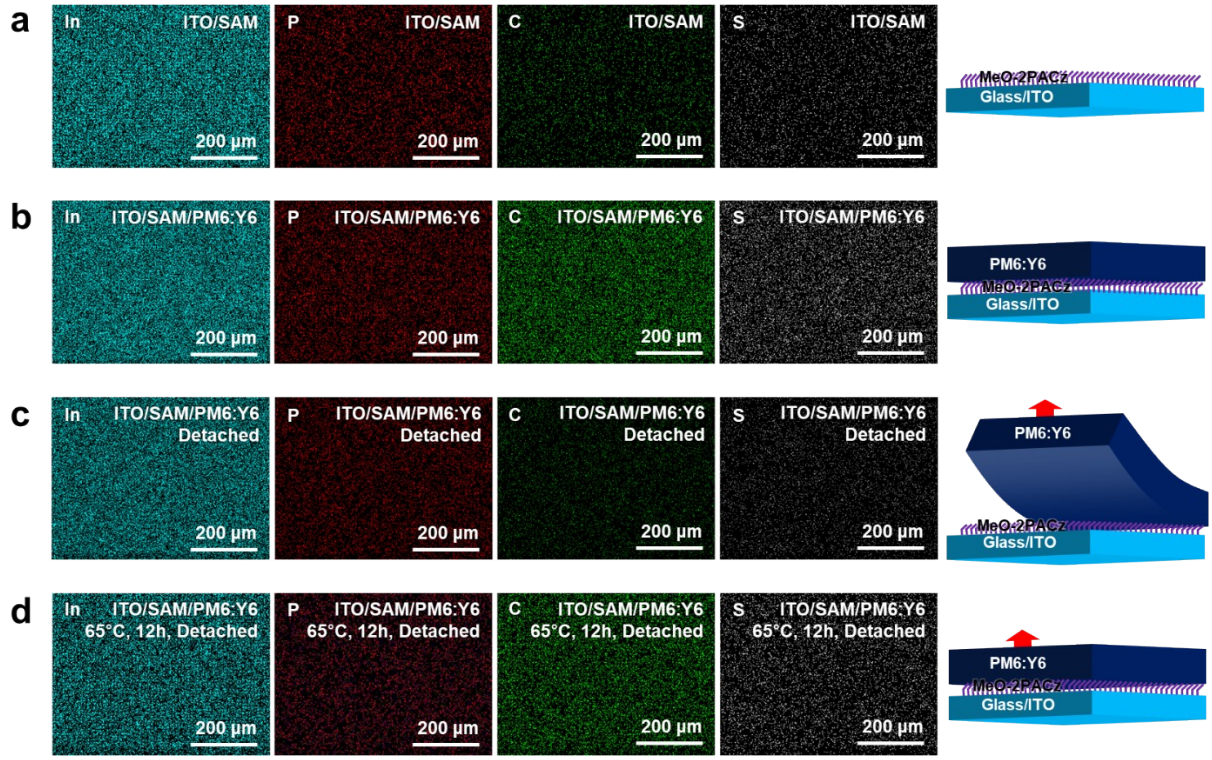

Figure S6. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping results of (a) pristine ITO/2MeO-2PACz, (b) pristine ITO/MeO-2PACz/PM6:Y6, (c) as-cast ITO/MeO-2PACz/PM6:Y6 film after peeling test, and (d) 65°C annealed ITO/MeO-2PACz/PM6:Y6 film after peeling test. The analysed elements, from left to right, are indium (In), phosphorus (P), carbon (C) and sulphur (S). For comparative interpretation, the color scale of each element map was normalized based on the indium (ITO) signal.

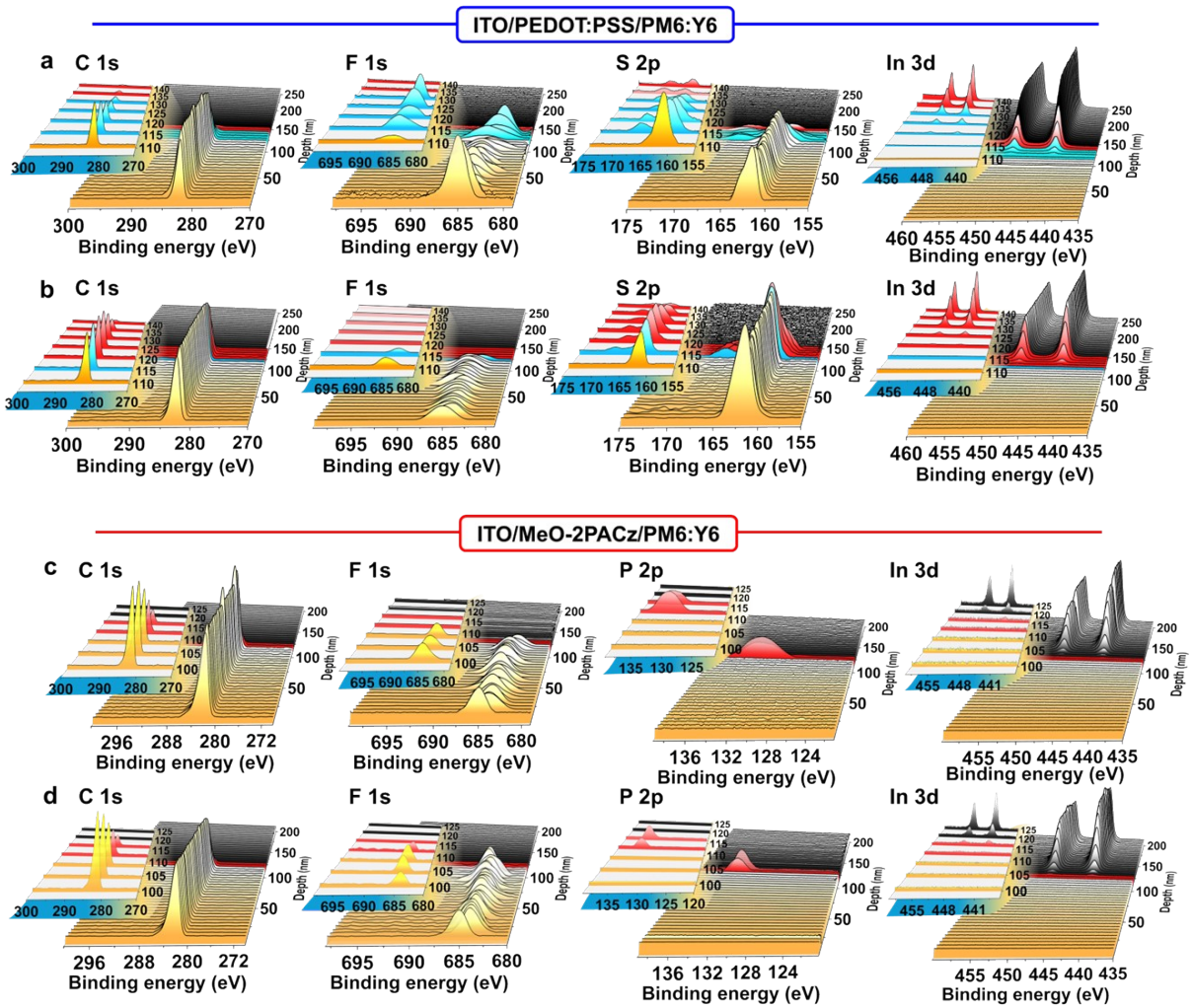

Figure S7. Depth profile XPS spectra of (a) pristine ITO/PEDOT:PSS/PM6:Y6 film, (b) annealed ITO/PEDOT:PSS/PM6:Y6 film at 65 °C for 12 hours, (c) pristine ITO/MeO-2PACz/PM6:Y6 film and (d) annealed ITO/MeO-2PACz/PM6:Y6 film at 65 °C for 12 hours.

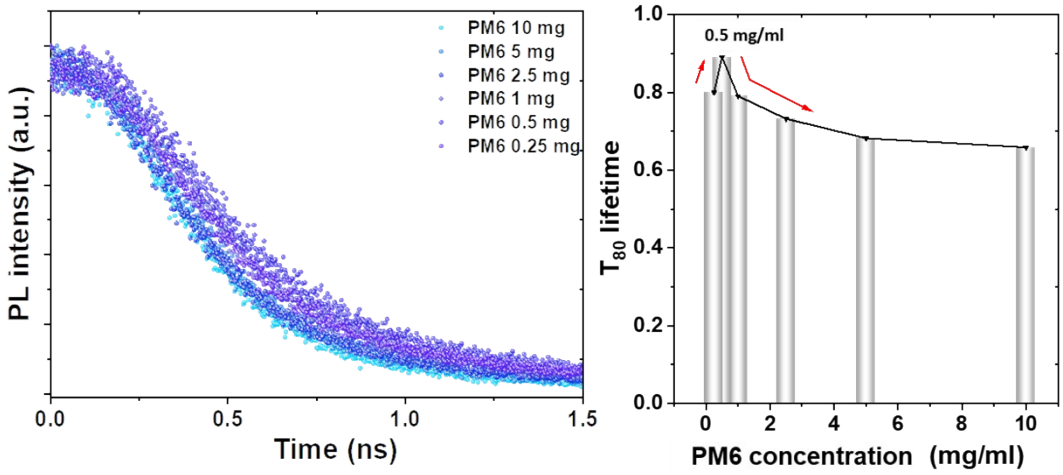

Figure S8. TRPL graph and T_{80} lifetime depending on PM6 concentration of 0.25, 0.5, 1, 2.5, 5 and 10 mg/ml in chloroform. The optimal concentration condition is 0.5 mg/ml.

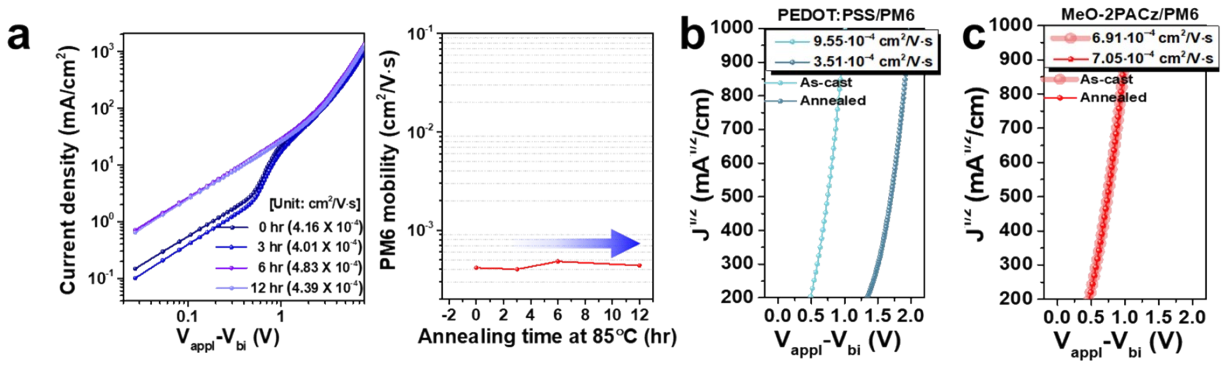

Figure S9. SCLC plots of (a) 0.5 mg/ml PM6 over aging time at 65 °C. SCLC plots of (b) as-cast and annealed PEDOT:PSS/PM6 and (c) as-cast and annealed MeO-2PACz/PM6 at 65 °C for 12 hours.

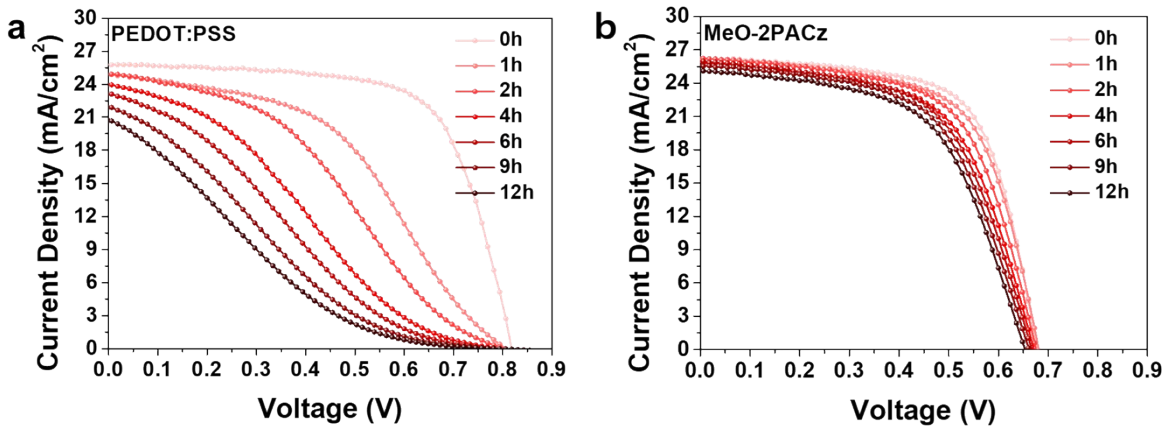

Figure S10. Time-dependent J–V curves of a representative device from the stability tests of ITO/HTL/PM6:Y6/PFN-Br/Ag structures using (a) PEDOT:PSS and (b) MeO-2PACz as the HTL.

Table S1. Contact angle of water and glycol and calculated surface energy from average contact angle values.

Sample		$\theta_{water,1}$	$\theta_{water,2}$	$\theta_{water,3}$	$\theta_{water, average}$	$\theta_{Glycerol,1}$	$\theta_{Glycerol,2}$	$\theta_{Glycerol,3}$	$\theta_{Glycerol, average}$	Surface E
Before annealing	Glass/PEDOT:PSS	19.7°	23.7°	19.4°	20.9°	58.5°	54.5°	55.8°	56.3°	131.9°
	ITO/MeO-2PACz	62.2°	63.2°	61.1°	62.2°	67.8°	67.6°	66.4°	67.3°	46.4°
	Glass/PM6:Y6	104.3°	104.3°	103.9°	104.2°	92.3°	91.5°	91.4°	91.7°	20.3°
After annealing	Glass/PEDOT:PSS	29.5°	29.3°	29°	29.3°	54.7°	50°	48.7°	51.1°	95.3°
	ITO/MeO-2PACz	58.2°	58.6°	59.1°	58.6°	71.1°	69.9°	69.8°	70.3°	60.7°
	Glass/PM6:Y6	106.1°	104.3°	105.9°	105.4°	89.2°	89.3°	90.5°	89.7°	26.8°

Table S2. Device efficiencies depending on HTL of 10 different devices with device structures of ITO/HTL/PM6:Y6/PFN-Br/Ag.

HTL	J_{SC} [mA/cm^2]	V_{OC} [V]	*FF* [%]	PCE [%]
MeO-2PACz	27.0 (26.6 ± 0.54)[a]	0.673 (0.671 ± 0.01) [a]	68.8 (67.6 ± 0.93) [a]	12.5 (12.0 ± 0.37) [a]
PEDOT:PSS	26.1 (25.9 ± 0.27) [a]	0.83 (0.824 ± 0.01) [a]	69.9 (69.1 ± 1.06) [a]	15.1 (14.7 ± 0.25) [a]

[a] The values in parentheses for each parameter are the average and standard deviation for 10 different devices.

Table S3. Raw data of PCE stability vs. annealing time for TO/HTL/PM6:Y6/PFN-Br/Ag devices using PEDOT:PSS or MeO-2PACz as HTL.

Anneal. Time	HTL	Device No.	J_{SC} [mA/cm^2]	V_{OC} [V]	FF [%]	PCE [%]	PCE Retention (%)
0 hour	**PEDOT:PSS**	1	26.5	0.818	62.9	13.62	**100**
0 hour	**PEDOT:PSS**	2	25.8	0.818	67.4	14.25	**100**
0 hour	**PEDOT:PSS**	3	26.2	0.818	68.3	14.63	**100**
0 hour	**PEDOT:PSS**	4	26.3	0.806	67.9	14.39	**100**
0 hour	**PEDOT:PSS**	5	26.2	0.806	63.5	13.4	**100**
0 hour	**MeO-2PACz**	1	26.4	0.673	66.0	11.72	**100**
0 hour	**MeO-2PACz**	2	26.6	0.673	66.3	11.87	**100**
0 hour	**MeO-2PACz**	3	26.2	0.685	65.9	11.83	**100**
0 hour	**MeO-2PACz**	4	26.3	0.673	65.9	11.65	**100**
0 hour	**MeO-2PACz**	5	26.7	0.697	65.1	12.11	**100**
1 hour	**PEDOT:PSS**	1	25.0	0.77	44.5	8.55	**62.8**
1 hour	**PEDOT:PSS**	2	24.9	0.806	45.3	9.10	**63.9**
1 hour	**PEDOT:PSS**	3	24.7	0.806	44.0	8.75	**59.8**
1 hour	**PEDOT:PSS**	4	24.1	0.794	45.1	8.63	**60.0**
1 hour	**PEDOT:PSS**	5	23.4	0.794	33.9	6.30	**47.0**
1 hour	**MeO-2PACz**	1	26.3	0.685	62.8	11.29	**96.3**
1 hour	**MeO-2PACz**	2	26.4	0.673	61.5	10.92	**92.0**
1 hour	**MeO-2PACz**	3	26.3	0.685	61.3	11.04	**93.3**
1 hour	**MeO-2PACz**	4	26.0	3673	63.1	11.05	**94.8**
1 hour	**MeO-2PACz**	5	26.1	0.697	62.8	11.43	**94.4**
2 hours	**PEDOT:PSS**	1	25.4	0.709	38.6	6.95	**51.0**
2 hours	**PEDOT:PSS**	2	25.0	0.806	36.5	7.36	**51.7**
2 hours	**PEDOT:PSS**	3	24.8	0.794	36.4	7.16	**49.0**
2 hours	**PEDOT:PSS**	4	23.4	0.794	37.1	6.91	**48.0**
2 hours	**PEDOT:PSS**	5	22.9	0.782	28.0	5.02	**37.5**
2 hours	**MeO-2PACz**	1	26.4	0.673	61.1	10.83	**92.4**
2 hours	**MeO-2PACz**	2	26.0	0.673	60.7	10.63	**89.6**

2 hours	**MeO-2PACz**	3	26.1	0.685	60.8	10.86	**91.8**
2 hours	**MeO-2PACz**	4	25.6	0.673	62.1	10.70	**91.8**
2 hours	**MeO-2PACz**	5	26.1	0.697	60.5	10.98	**90.7**
4 hours	**PEDOT:PSS**	1	23.7	0.661	29.9	4.68	**34.3**
4 hours	**PEDOT:PSS**	2	24.1	0.794	27.7	5.30	**37.2**
4 hours	**PEDOT:PSS**	3	23.9	0.794	26.2	4.97	**34.0**
4 hours	**PEDOT:PSS**	4	22.3	0.782	26.8	4.67	**32.4**
4 hours	**PEDOT:PSS**	5	22.4	0.782	34.7	6.07	**45.3**
4 hours	**MeO-2PACz**	1	26.0	0.673	59	10.31	**88.0**
4 hours	**MeO-2PACz**	2	26.0	0.661	59.2	10.16	**85.6**
4 hours	**MeO-2PACz**	3	26.2	0.673	60.7	10.69	**90.4**
4 hours	**MeO-2PACz**	4	25.7	0.673	59.8	10.35	**88.8**
4 hours	**MeO-2PACz**	5	26.3	0.685	60.0	10.79	**89.1**
6 hours	**PEDOT:PSS**	1	22.7	0.624	26.2	3.71	**27.2**
6 hours	**PEDOT:PSS**	2	23.2	0.782	24.0	4.353	**30.5**
6 hours	**PEDOT:PSS**	3	23.1	0.782	22.1	3.99	**27.3**
6 hours	**PEDOT:PSS**	4	21.5	0.782	22.5	3.782	**26.3**
6 hours	**PEDOT:PSS**	5	21.3	0.661	33.9	4.77	**35.6**
6 hours	**MeO-2PACz**	1	26.0	0.673	57.4	10.05	**85.8**
6 hours	**MeO-2PACz**	2	25.9	0.661	58.3	9.96	**83.9**
6 hours	**MeO-2PACz**	3	25.2	0.673	58.3	9.87	**83.4**
6 hours	**MeO-2PACz**	4	25.5	0.661	59.7	10.05	**86.3**
6 hours	**MeO-2PACz**	5	26.0	0.685	58.7	10.44	**86.2**
9 hours	**PEDOT:PSS**	1	21.3	0.624	21.9	2.90	**21.3**
9 hours	**PEDOT:PSS**	2	22.1	0.782	20.0	3.44	**24.2**
9 hours	**PEDOT:PSS**	3	21.4	0.782	17.9	3.00	**20.5**
9 hours	**PEDOT:PSS**	4	20.3	0.782	18.0	2.86	**19.9**
9 hours	**PEDOT:PSS**	5	20.5	0.624	26.3	3.37	**25.1**
9 hours	**MeO-2PACz**	1	25.7	0.661	57.4	9.75	**83.2**
9 hours	**MeO-2PACz**	2	25.5	0.648	56.7	9.37	**79.0**
9 hours	**MeO-2PACz**	3	25.5	0.661	57.5	9.69	**81.9**
9 hours	**MeO-2PACz**	4	24.9	0.661	57.4	9.43	**80.9**
9 hours	**MeO-2PACz**	5	25.5	0.673	58.3	10.01	**82.7**
12 hours	**PEDOT:PSS**	1	19.5	0.588	19.2	2.20	**16.1**
12 hours	**PEDOT:PSS**	2	21.0	0.782	17.2	2.83	**19.8**
12 hours	**PEDOT:PSS**	3	20.0	0.794	15.0	2.38	**16.3**
12 hours	**PEDOT:PSS**	4	18.4	0.794	14.7	2.15	**14.9**
12 hours	**PEDOT:PSS**	5	18.7	0.588	22.0	2.42	**18.1**
12 hours	**MeO-2PACz**	1	25.1	0.648	57.5	9.36	**79.9**
12 hours	**MeO-2PACz**	2	25.5	0.648	56.0	9.27	**78.1**
12 hours	**MeO-2PACz**	3	24.6	0.661	56.3	9.14	**77.2**
12 hours	**MeO-2PACz**	4	24.2	0.648	57.6	9.03	**77.5**
12 hours	**MeO-2PACz**	5	24.9	0.673	55.8	9.36	**77.3**