Supporting Information

Augmenting n-type Performance of ambipolar Top-Contact Organic Thin-film Transistors by Self-generated Interlayers

Tanmoy Sarkar[†], Jane Vinokur[†], Basel Shamieh[†], Victoria Savikhin[#‡], Michael F. Toney[#] and Gitti L. Frey [†]*

[†]Department of Materials Science and Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

[#]SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Building 137, Menlo Park, California 94025, United States

[‡]Electrical Engineering Department, Stanford University, 350 Serra Mall, Stanford, CA 94305, United States

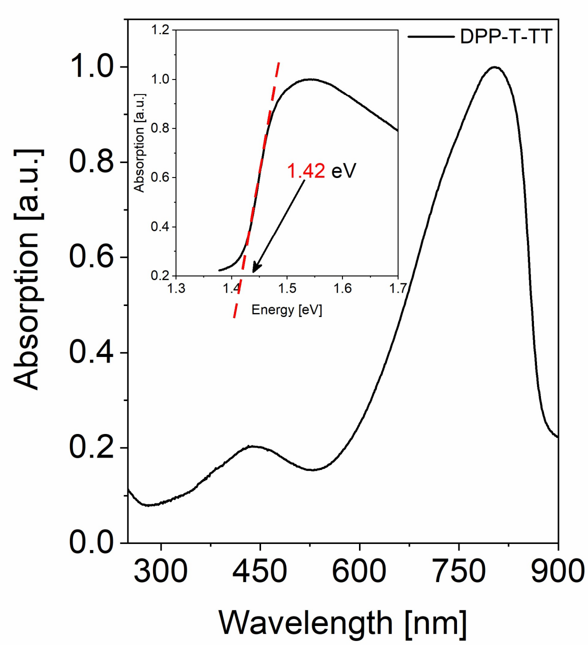

Figure S1: Absorption spectrum of a pristine DPP-T-TT film on quartz. Inset shows the onset of the absorption spectrum and corresponding extrapolation for band-gap value extraction. (Measurement performed using a Varian Cary 100 scan UV−vis spectrophotometer).

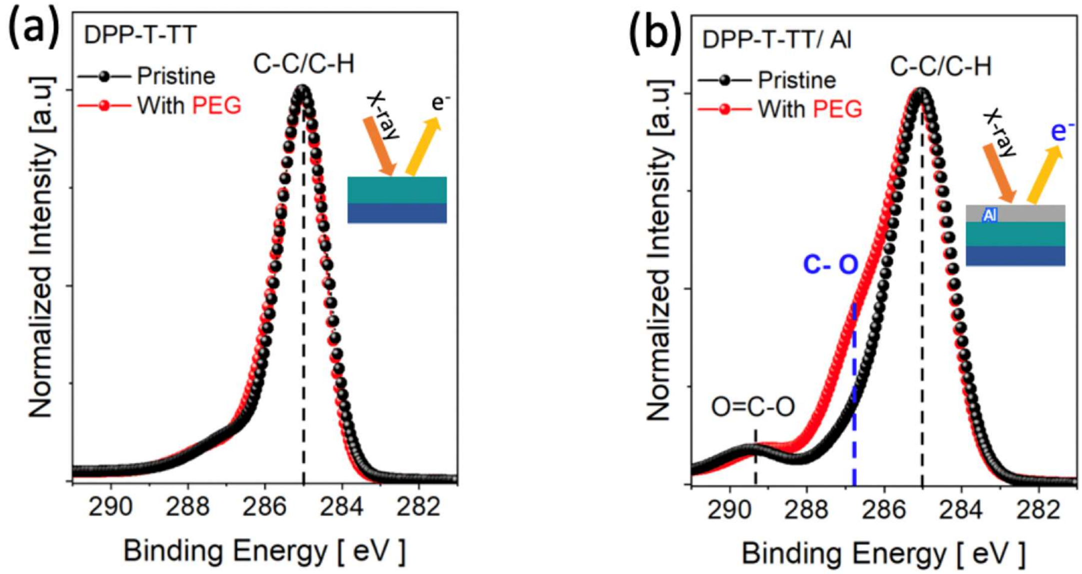

Figure S2: For the XPS measurements, we prepared two sets of DPP-T-TT polymer films: pristine and with PEG additive. Both films were partly covered with 3-4 nm Al layer and XPS measurements were performed on a bare region (not covered by Al) and an Al-covered region of each film, as schematically shown in the insets. Figure S2a shows the XPS spectra of the bare regions of pristine DPP-T-TT (black circles) and DPP-T-TT:PEG (red circles) films. Both spectra are identical and show a main C1s peak at 285 eV, characteristic of the C- C/C-H bonds of the polymer. There is no evidence of the PEG characteristic C-O bond expected at 286.45 eV, at the polymer/air interface.[1] Figure S2b shows the XPS spectra of the Al covered regions of pristine DPP-T-TT (black circles) and DPP-T-TT:PEG (red circles) films. The spectrum of the Al-coated pristine DPP-T-TT (black circles) is similar to that of the bare regions with a weak contribution at around 287.4 eV associated with minor O–C=O contaminations. In contrast, the XPS spectrum of the Al-coated region of DPP-T-TT:PEG (red circles) shows a noticeable contribution at 286.6 eV associated with the C-O characteristics peak of PEG. The C-O fingerprint of PEG molecule exclusively present at the Al/polymer interface unambiguously confirm migration of PEG molecules to the Al/polymer interface and the self-generation of a PEG interlayer at the organic/Al interface.

Equation- S1: The saturation mobility (μ_{sat}) is calculated using the following equation: [2]

$$\mu_{Sat} = \frac{2L\left(\frac{\sqrt{I_{Drain}}}{V_{Gate} - V_{Th}}\right)^2}{WC}$$

Where, W, L, and C are the transistor channel width, channel length, and capacitance of the gate insulator per unit area, respectively. I_{Drain}, V_{Gate}, and V_{Th} are the measured drain-to-source current, gate-to-source voltage, and threshold voltage measured from the transfer characteristics, respectively.

Equation- S2: Field-effect mobility (μ_{eff}): Obtained by the transconductance (g_m) with V_{Drain}:[3]

$$\mu_{eff} = \frac{g_m}{C\frac{W}{L}V_{Drain}}$$

Equation- S3: Change in electron density estimated by parallel capacitance model leads to derivation of the relationship:[4]

$$\Delta n_e = C\,\Delta V_{Th}/e$$

Where, ΔV_{Th} is the threshold voltage difference of the devices and e is the elementary charge.

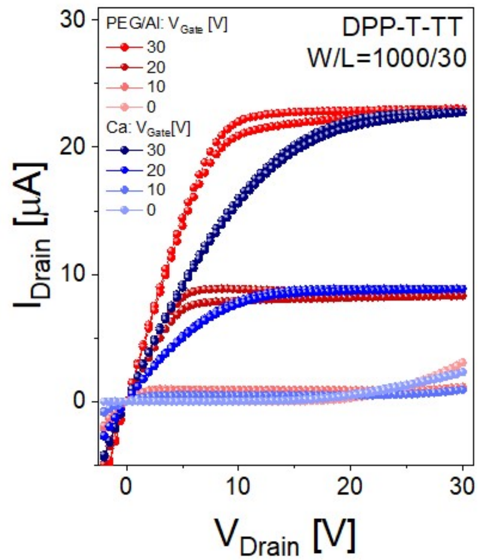

Figure S3. Output characteristics comparison of Ca/Al device and PEG/Al devices.

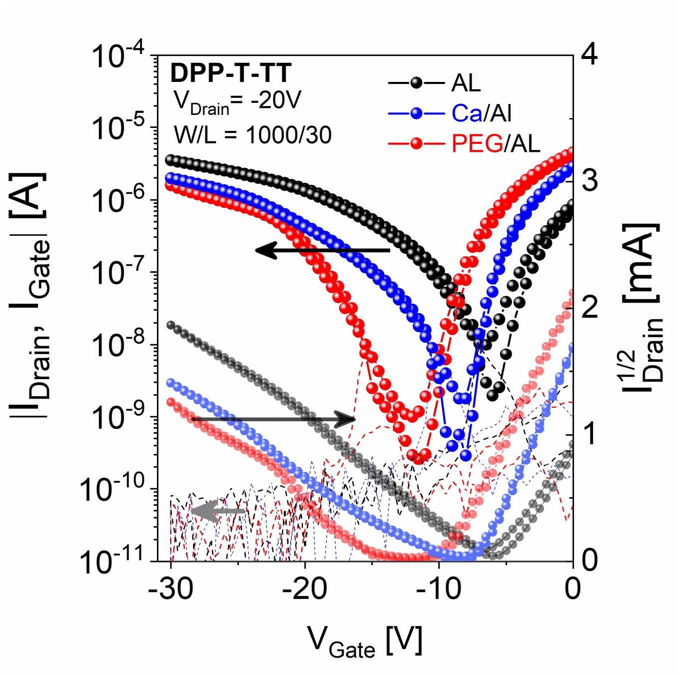

Figure S4: p-type Transfer characteristics of the DPP-T-TT OFETs on Si-SiO_2 substrate with Al contacts with (red circles) and without (black circles) PEG at V_{Drain} = -20V for W/L=1000/30. The dashed lines show the corresponding gate currents of each of the devices.

Table T1: Summary of n-channel characteristics of the transistors fabricated in this study:

DPP-T-TT	Mobility [$cm^2\ v^{-1}\ s^{-1}$]	V_{Th} [V]	V_{ON} [V]	R_c.W [KΩ.cm]	$R_{channel}$.W [KΩ.cm]
Pristine	0.03 ± 0.015	16.1	11 ±1	209 ±50	2.03
With PEG	0.22 ±0.04	10	5 ±0.5	51 ±10	1.31
With Ca	0.16±0.02	8.8	8±1	86±21	1.30±0.5

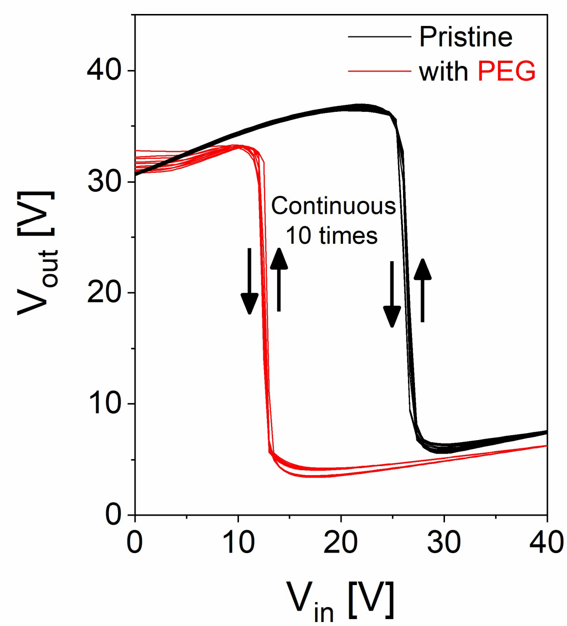

***Figure S5**:* Stability characterization by 10-continuous voltage-transfer scans of inverter devices based on two identical OFETs, with PEG (red lines) and without PEG (black lines).

Table T2: Calculated values extracted from the GIWAXS analysis:

	Alkyl Q	d-spacing [A]	(100) Alkyl peak area (x10^3)	(200) Alkyl peak area (x10^3)	Amorphous peak area OOP (x10^3)	Amorphous peak area IP (x10^3)	Alkyl peak FWHM (A^{-1})
DPPT-TT: PEG bulk	0.315, 0.62	19.95	2.8	0.195	4	3.55	0.049
DPPT-TT bulk	0.315, 0.62	19.95	3.5	0.233	4.2	3.72	0.043
DPPT-TT:PEG surface	0.32, 0.625, 0.93, 1.25	19.63	16	1.37	-	-	0.048
DPPT-TT surface	0.315, 0.615	19.95	4.7	0.56	-	-	0.047

REFERENCES

1. Shamieh, B.; Obuchovsky, S.; Frey, G. L., Spontaneous generation of interlayers in OPVs with silver cathodes: enhancing Voc and lifetime. *Journal of Materials Chemistry C* **2016,** 4, (9), 1821-1828.
2. Sarkar, T.; Shamieh, B.; Verbeek, R.; Kronemeijer, A. J.; Gelinck, G. H.; Frey, G. L., Tuning Contact Resistance in Top-Contact p-Type and n-Type Organic Field Effect Transistors by Self-Generated Interlayers. *Advanced Functional Materials* **2019,** 0, (0), 1805617.
3. Fortunato, E.; Barquinha, P.; Martins, R., Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. *Advanced Materials* **2012,** 24, (22), 2945-2986.
4. Roh, J.; Lee, T.; Kang, C.-m.; Kwak, J.; Lang, P.; Horowitz, G.; Kim, H.; Lee, C., Injection-modulated polarity conversion by charge carrier density control via a self-assembled monolayer for all-solution-processed organic field-effect transistors. *Scientific Reports* **2017,** 7, 46365.