

Supporting Information

Enhanced Self-Assembled Monolayer Treatment on Polymeric Gate Dielectrics with Ultraviolet/ozone Assistance in Organic Thin Film Transistor

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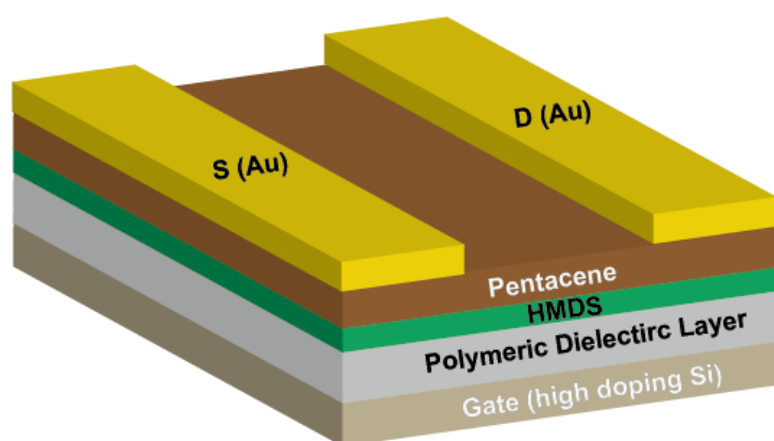


Figure S1. Configuration of pentacene based top-contact bottom-gate OFETs with HMDS modification.

Saturation mobility can be extracted from the slope of the plot of $|I_{DS}|^{1/2}$ versus V_{GS} at $V_{DS} = -40$ V from the equation, $I_{DS} = (WC_i/2L) \mu (V_{GS} - V_T)^2$ in the transfer curves. Where W is the device channel width, L is the device channel length, C_i is the capacitance per unit area of the gate dielectric and V_T is threshold voltage. The threshold voltage is the V_{GS} when the channel conductance (at low V_{DS}) is equal to that of the whole semiconducting film, which corresponds to the extrapolation of the line to zero current.

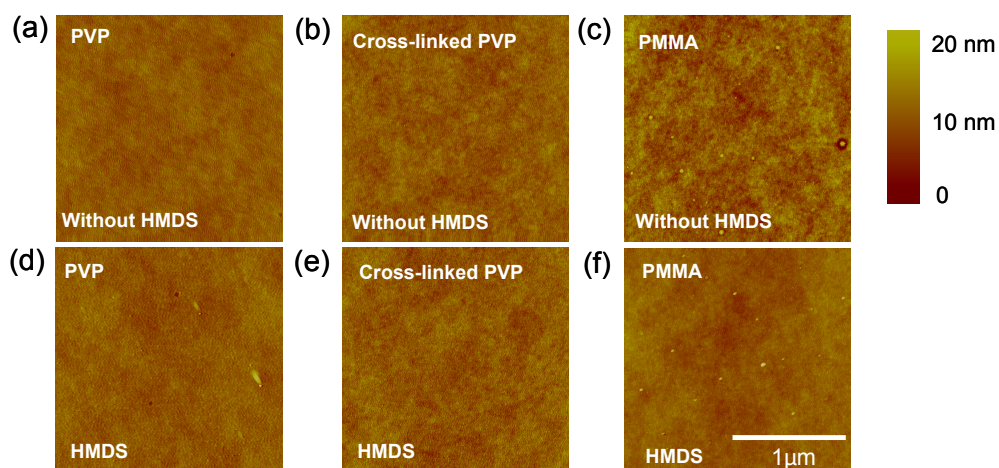


Figure S2. Tapping mode AFM height image of various polymer surfaces: (a, d) PVP (b, e) Cross-linked PVP, (c, f) PMMA, without or with HMDS modification.

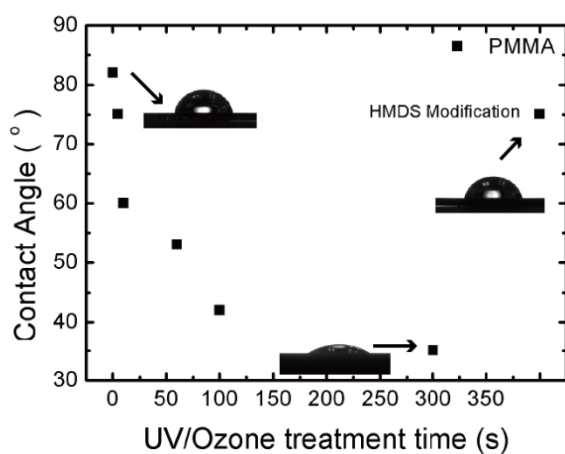


Figure S3. The contact angle change with UV/ozone exposure time for PMMA sample.

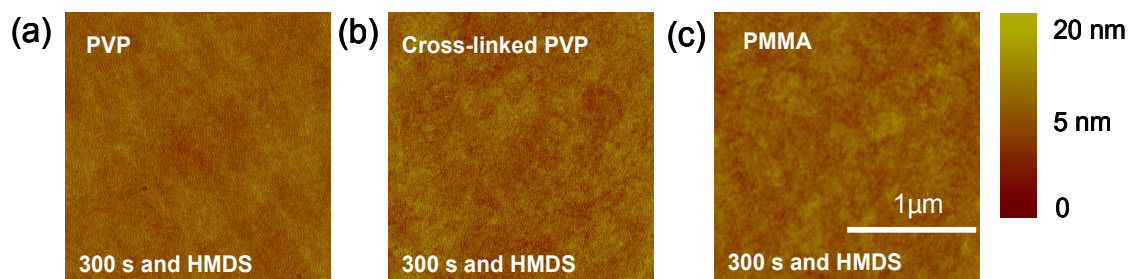


Figure S4. Tapping mode AFM height image of various polymer surfaces: (a) PVP (b) Cross-linked PVP, (c) PMMA, with 300 s UV/ozone exposure and HMDS modification.

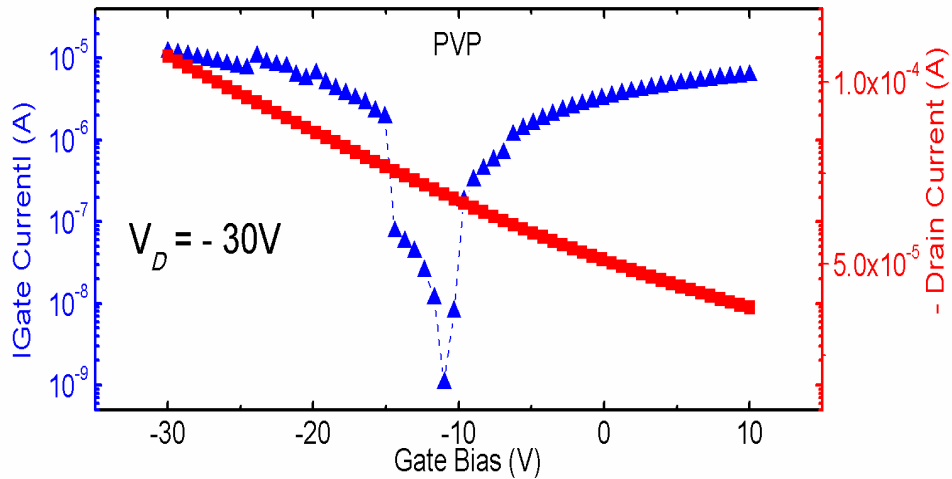


Figure S5. Transfer characteristics and gate current dependence of gate bias in OTFT: PVP substrate after 300 s UV/ozone exposure and HMDS modification

Figure S5 shows the transfer characteristics and gate current dependence of gate bias in OTFT. The device used PVP as dielectric insulator treated with 300 s UV/ozone exposure and HMDS modification. UV/ozone exposure changes the insulator properties of PVP dielectrics, resulting high leakage current (10^{-5} A) and the device could not be switched off completely. These results demonstrate that the long period UV/ozone exposure leads to the degeneration of device electrical performance.

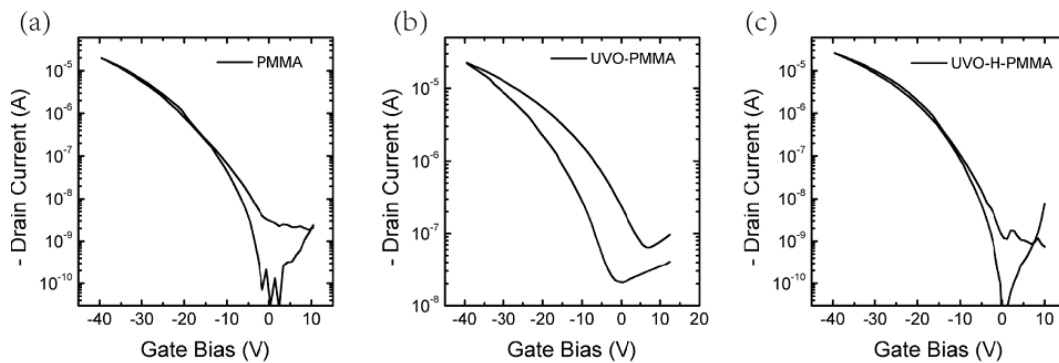


Figure S6. Hysteresis in the transfer characteristics of the OFETs with PMMA, UV/ozone treated PMMA and UV/ozone-HMDS treated PMMA

Figure S6 shows the hysteresis in the transfer characteristics of the OFETs with PMMA, UVO-PMMA and UVO-H-PMMA. The transfer curves scanned from 10 to -40 V and then from -40 to $+10$ V and all the I-V characteristics are measured in the air. We can find that no significant hysteresis effect for PMMA based device. However, the UVO-PMMA based device exhibited a large hysteresis. As we known,

the OH groups at the gate dielectric/semiconductor interface are essential to hysteresis problem.^{1,2} As the PMMA layer is free of OH groups, the hysteresis can be effectively avoided. However, with the increase of OH groups due to UV/Ozone treatment, the electron trappings related to the hydroxyl groups is enhanced, contributing to increased hysteresis. For the devices with HMDS modification, the hydroxyl groups is further decreased in the semiconductor/ dielectric interface due to chemical bonding with HMDS molecular, showing a less hysteresis in the transfer cures as shown in Figure 3c.

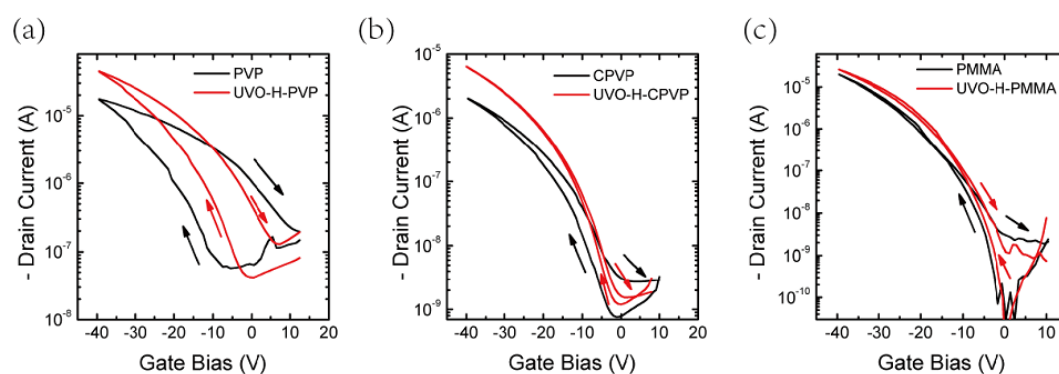


Figure S7. Hysteresis measurement for OFETs with various polymeric dielectrics.

Figure S7 shows the transfer curves scanned from 10 to -40 V and then from -40 to $+10$ V for the device with various polymeric dielectric layer. As the moisture is considered as the root cause of the hysteresis problem for the OFETs with a polymeric dielectric layer, all the I-V characteristics are measured in the air. We can find that the PVP based device exhibited a large hysteresis, while a reduced hysteresis is observed for CPVP based device. The OH groups in the bulk and at the gate dielectric/semiconductor interface are essential to hysteresis problem.^{1, 2} The cross-linked process for the fabrication of CPVP film can minimize the hydroxyl groups, contributing to reduced hysteresis. For the devices with HMDS modification, the hydroxyl groups is further decreased in the semiconductor/ dielectric interface, showing a less hysteresis in the transfer cures. The transfer curve of PMMA based devices show almost no hysteresis. As the PMMA layer is free of OH groups, the influence of moisture can be effectively avoided.

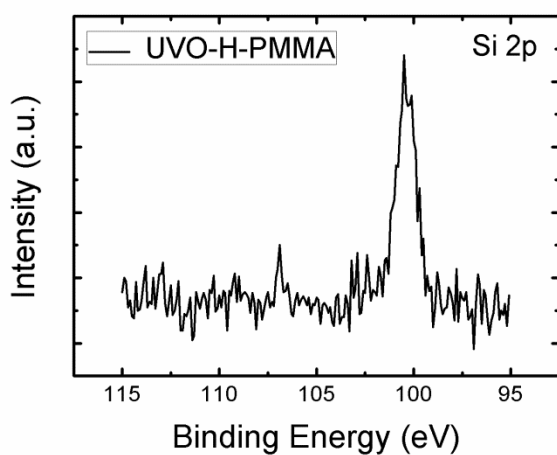


Figure S8. XPS spectra of UVO and HMDS treatment polymer dielectric film: UVO-H-PMMA.

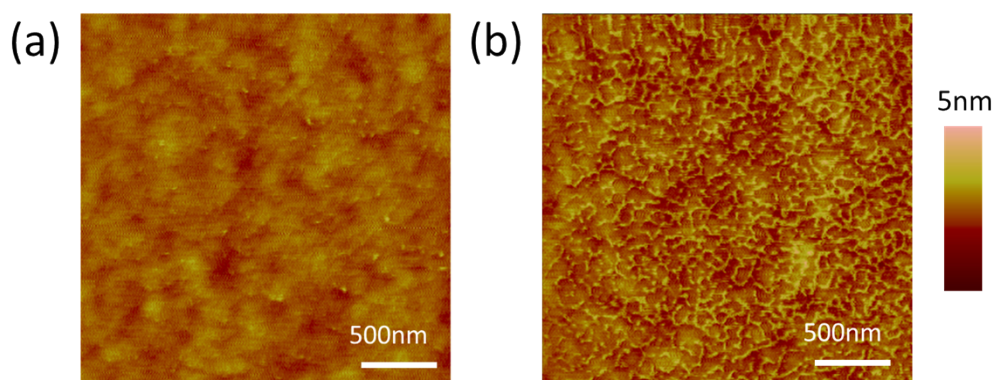


Figure S9. Tapping mode AFM height image of HMDS monolayers: (a) PVP with 10 s and HMDS modification (b) PVP with 300 s UV/ozone exposure and HMDS modification.

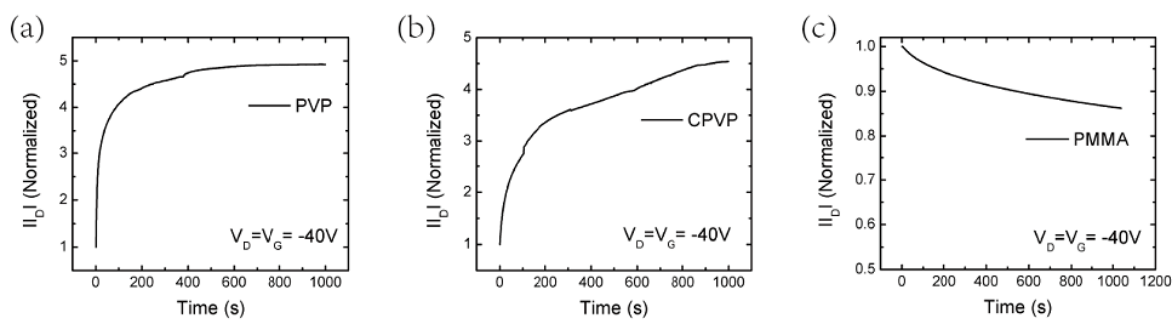


Figure S10. Bias stress experiments for OFETs with various polymeric dielectrics.

Figure S10 shows the result of bias stress experiments. In the case of OFETs with PVP and CPVP dielectric layer, the channel current increase with the time. The increased current is attributed to the slow depolarization for dielectric layer.^{3, 4} However, in the case of PMMA-type OFETs, the drain current gradually reduces with time, probably because the trapping/detrapping of electrons in the pentacene/PMMA interface. The current stability of OFETs with HMDS modification is also measured, not showing an obvious depressing and result is not shown here.

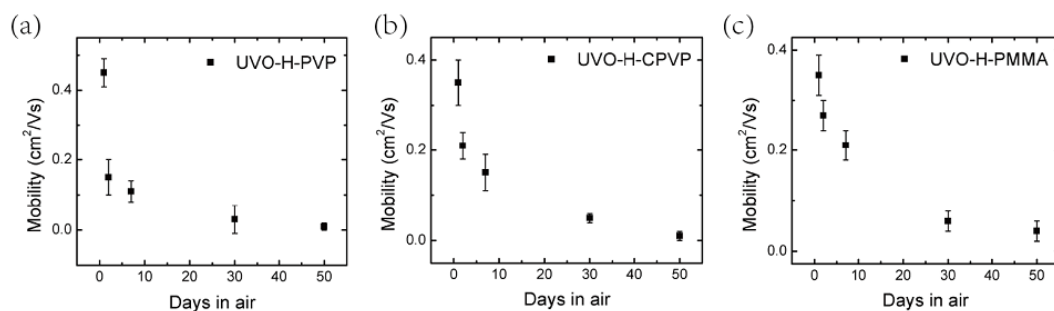


Figure S11. Air stability measurement of OFETs based on various polymeric dielectrics.

Figure S11 shows air stability measurement of OFETs based on UVO-H-PVP, UVO-H-CPVP and UVO-H-PMMA polymeric dielectric layers. The devices have been exposed to ambient air for 50 days with humidity around 50%. The mobility of UVO-H-PVP based transistors shows a more obvious degenerate compared with UVO-H-PMMA based devices in the first 7 days. It is probable because the devices are much easier to be influenced by the water in air due to the rich OH groups in the PVP bulk region. Meanwhile, after 50 days of continuous exposure in air, all the mobilities of devices decrease by an order of magnitude.

| <i>Type</i> | <i>HMDS</i> | <i>RMS</i> (Å) | $-V_{Th}$ (V) | μ_p (cm ² /Vs) | <i>Grain size</i> (μm) | <i>On/off ratio</i> | <i>CA</i> (°) |
|-------------|-------------|-------------------|------------------|----------------------------------|---------------------------|----------------------------------|------------------|
| PVP | × | 2.6-2.9 | 7-10 | 0.05-0.08 | 0.41-0.43 | 10 ⁴ -10 ⁵ | 63 |
| PVP | ✓ | 3.1-3.5 | 5-8 | 0.21-0.30 | 0.66-0.71 | 10 ⁵ -10 ⁶ | 73 |
| CPVP | × | 2.3-2.7 | 16-20 | 0.04-0.07 | 0.25-0.28 | 10 ³ -10 ⁴ | 78 |
| CPVP | ✓ | 3.0-3.5 | 10-12 | 0.13-0.18 | 0.58-0.63 | 10 ⁵ -10 ⁶ | 76 |
| PMMA | × | 4.0-4.3 | 20-25 | 0.20-0.27 | 0.36-0.42 | 10 ⁴ -10 ⁵ | 82 |
| PMMA | ✓ | 4.1-4.3 | 16-20 | 0.25-0.30 | 0.34-0.43 | 10 ⁴ -10 ⁵ | 80 |

Table S1. The performance of field-effect mobilities, threshold voltages, on/off ratio in the OTFTs and root-mean-square, pentacene grain size, contact angle of polymer substrate samples with/without HMDS treatment.

| <i>Type</i> | <i>HMDS</i> | <i>Uv/ozne</i> (s) | <i>RMS</i> (Å) | $-V_{Th}$ (V) | μ_p (cm ² /Vs) | <i>Grain size</i> (μm) | <i>On/off ratio</i> | <i>CA</i> (°) |
|-------------|-------------|-----------------------|-------------------|------------------|----------------------------------|---------------------------|----------------------------------|------------------|
| PVP | ✓ | 10 | 3.7-4.1 | 5-9 | 0.43-0.47 | 0.90-1.1 | 10 ⁵ -10 ⁶ | 74 |
| PVP | ✓ | 300 | 3.3-3.7 | / | / | 0.33-0.37 | / | 57 |
| CPVP | ✓ | 10 | 2.7-3.3 | 7-10 | 0.32-0.37 | 0.65-0.75 | 10 ⁵ -10 ⁶ | 73 |
| CPVP | ✓ | 300 | 3.2-3.6 | 7-11 | 0.011-0.018 | 0.13-0.15 | 10 ² -10 ³ | 66 |
| PMMA | ✓ | 10 | 4.2-4.5 | 15-20 | 0.12-0.16 | 0.33-0.37 | 10 ⁴ -10 ⁵ | 76 |
| PMMA | ✓ | 300 | 4.1-4.5 | 18-23 | 0.0008-0.0019 | 0.17-0.21 | 10 ¹ -10 ² | 75 |

Table S2. The performance of field-effect mobilities, threshold voltages, on/off ratio in the OTFTs and root-mean-square, pentacene grain size, contact angle of polymer substrate samples with short/long UVO exposure time (all the samples are modified with HMDS monolayer).

- [1] S. C. Lim, S. H. Kim, J. B. Koo, J. H. Lee, C. H. Ku, Y. S. Yang, T. Zyung, *Applied Physics Letters* 2007, **90**, 173512.
- [2] Se Hyun Kim, J. Jang, H. Jeon, W. M. Yun, S. Nam, C. E. Park, *Applied Physics Letters* 2008, **92**, 183306.
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- [4] D. K. Hwang, K. Lee, J. H. Kim, S. Im, J. H. Park, E. Kim, *Applied Physics Letters* 2006, **89**, 093507.