Supporting Information

Quantitative Characterization of Interface Stress Using Nanoindentation Technique for High Performance Flexible Electronics

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Film preparation

Cross-linked Poly(4-vinylphenol): Poly(4-vinylphenol) (PVP) was dissolved in PGMEA with concentration of 150 mg/ml, and then cross-linker called HDA was added into the solution with ratio of 15 mg/ml. Finally, the prepared cross-linked PVP solution was stirred by using a magnetic spin bar at room temperature for 24 hours. The cross-linked PVP film was formed via the described spin-coating procedure. The cross-linker solution was filtered through a 0.22 um membrane filter, then spin-coated at 600 rpm for 5 s, and 2000 rpm for 30 s onto the substrate, subsequently the PVP films (gate insulator) were thermally cross-linked for 2 hours at 120 °C in the glove box filled with nitrogen (H_2O<0.1 ppm, O_2<0.1 ppm). The resulting device capacitance was 3.80 nF cm^{-2} on the PET substrate, and the thickness of film was 850 nm measured by profilometer.

Cross-linked PVP film modification: According to the request of the research, cross-linked PVP film was modified with two different kinds of methods: UV-ozone treatment and self-assembled monolayer (OTS) modification. UV-ozone treatment: after the cross-linked PVP film formed, the sample was exposed to gentle UV-ozone treatment for five minutes. OTS modification: 50 ul octadecylsilane solution was heated at 100 °C for promotion evaporation, and then prepared cross-linked film was exposed to octadecylsilane vapour for 15 minutes. After that, the sample rinsed with toluene by spin-coating at 2000 rpm for 30 s and then annealed at 60 °C for 10 minutes to promote monolayer formation.

CYTOP: CYTOP films were made from a commercially available CYTOP solution, which consists of CTL-809M(solute) and CT-Solv.180(solvent). In our work, the CYTOP solution was made from the mixture of CTL-809M and CT-Solv.180 at weight ratio of 1:0. After the solution prepared, it was kept in the dark environment. Before spin-coating the gate insulator, CYTOP

solution was preheated at 80 °C for 30 minutes. The CYTOP film was formed by spin-coating at 2000 rpm for 60 s, and then annealed at 110 °C for 60 minutes. The resultant device capacitance was 2.18 nF cm^{-2} on the PET substrate, and the thickness of film was 804 nm measured by profilometer. CYTOP owns the hydrophobic surface, so the film should be treated with gentle UV-ozone for 10 minutes before the spin-coating of semiconductor layer to ensure uniform film.

PVA: Polyvinyl alcohol was dissolved in deionized water with a concentration of 60 mg/ml, and then the solution was heated at 100 °C for 3 hours to get homogeneous solution. Before the PVA film was spin-coated, the solution should be preheated at least 30 minutes to obtain uniform film. The solution was filtered through a 0.45 um membrane filter before the PVA film was formed via the described spin-coating process at 1000 rpm for 60 s and cured at 100 °C for 60 minutes under nitrogen environment. The capacitance of resultant device was 8.05 nF cm^{-2} on the PET substrate, and the thickness of film was 734 nm measured by profilometer.

PDVT-8: PDVT-8 was dissolved in chloroform at ratio of 10 mg/ml, which was spin-coated on gate insulator at 1000 rpm for 60 s and then annealed at 150 °C for 10 minutes to form uniform p-type semiconductor film and the average thickness of the film was about 100 nm for different interface adhesion energy.

Bending deformation measurement

To study the effects of interface stress on the mechanical and electrical characteristics of the flexible OFETs, plastics rings with different bending radius (∞, 50 mm, 25 mm, 15 mm and 5 mm, the radius of ∞ means flat) was introduced and flexible devices electrical performance was then characterized under different bending conditions with the bending direction perpendicular to the source and drain electrodes. Meanwhile, the bending cycles test was conducted with fixed radius of

15 mm up to 200 times.

Characterization

The electrical characteristics of flexible OFET were measured using an Agilent B2902 semiconductor parameter analyzer. The capacitance (C_i) of dielectric layer was performed with an Agilent E4980A LCR meter, and the experiment was carried out by using the metal-insulator-metal (MIM) capacitor. Contact angle measurements were taken using Kino SL200KS. The thickness of dielectric layers was evaluated with the profilometer (Bruker Daktak-XT). UV-ozone treatment was carried out by the machine called HW10171601A. Nanoindentation tests on load-displacement curves were obtained using Nano-indenter NHT3 (made by Anton Paar). All measurements were carried out under ambient condition.

As we all known, interface modification would affect insulator/semiconductor interface adhesion energy, and adhesion energy between gate insulator and semiconductor was calculated by following equation:[1]

$$E_{ad_{i,j}} = 2\sqrt{r_i r_j}\,exp(-\beta(r_i - r_j)^2) \tag{S1}$$

Here, the emperical constant $\beta=1.247\times10^{-4}m^4mJ^{-2}$, and r_i, r_j respectively represents the surface free energy of dielectric layer and semiconductor layer.

To investigate the influence of interface stress on the stability of flexible OFET, the transfer characteristic curves of flexible OFETs were measured. The field-effect mobility in saturation region (μ_{sat}) was obtained from the following equation:[2,3]

$$\mu_{sat} = \frac{2L}{WC_i}\left(\frac{\partial\sqrt{I_{SD}}}{\partial V_G}\right)^2 \tag{S2}$$

where C_i is the capacitance per unit area of dielectric layer, measured with the capacitor structure of

MIM at 100 KHZ. L and W are the channel length and width, respectively.

Moreover, to examine the quality of semiconductor/dielectric interface, the interfacial trap density value (N_t) was calculated from the following equation:[4]

$$N_t = \frac{C_i}{q}\left[SS\frac{log(e)}{KT/q} - 1 \right] \quad \text{(S3)}$$

where q is the electron charge, SS is the sub-threshold slope, e is the base of the natural logarithm, K is the Boltzmann's constant, and T is the absolute temperature.

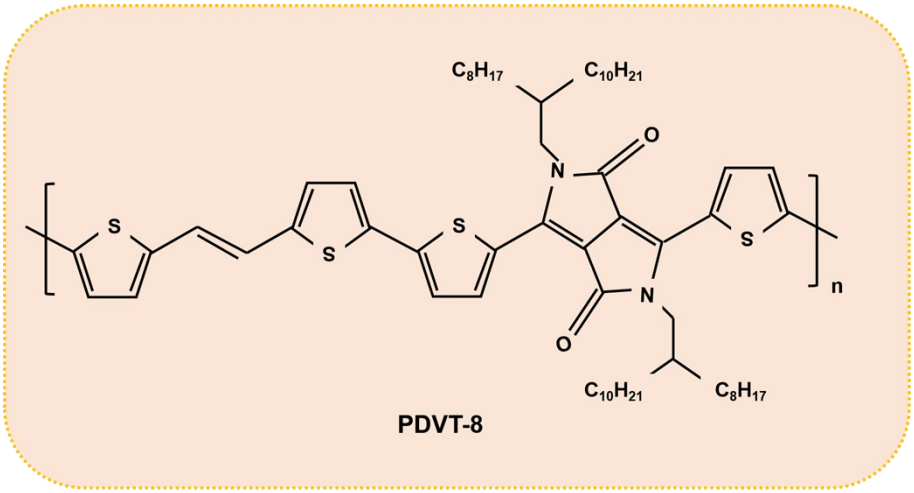

Fig. S1 Chemical structure of PDVT-8.

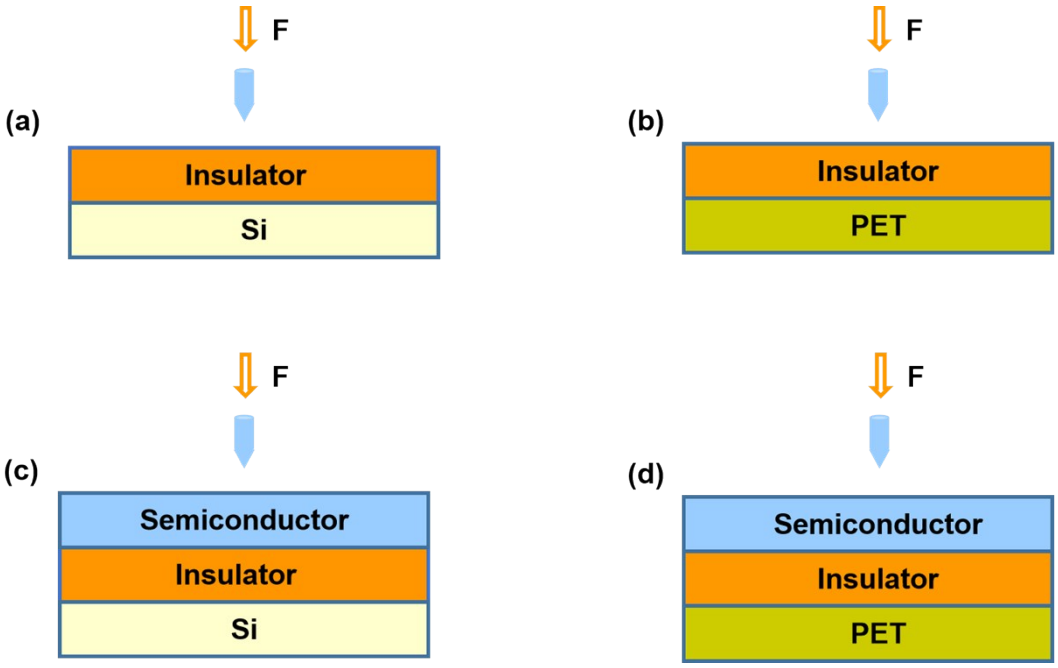

Fig. S2 The schematic of (a) the stress-free nanoindentation specimen of insulator/Si, (b) the stressing of insulator/PET, (c) the stress-free of PDVT-8/insulator/Si and (d) the stressing of PDVT-8/insulator/PET.

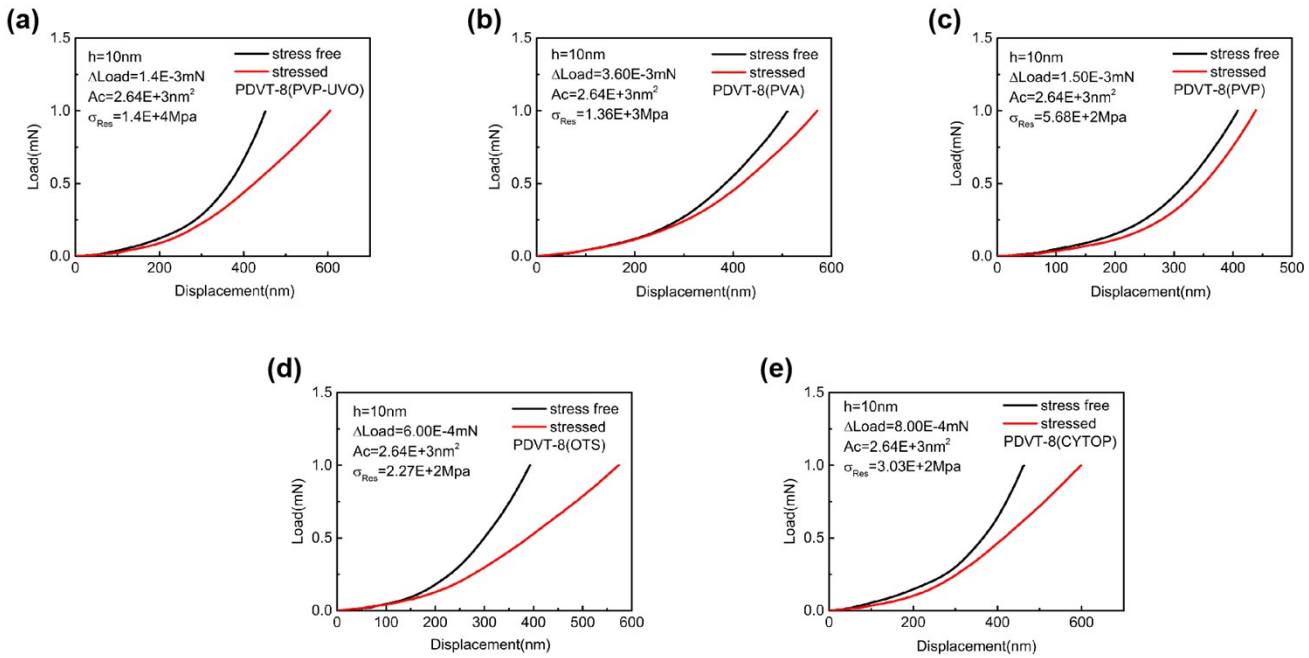

Fig. S3 Load-displacement curves of PDVT-8 film spin-coated on (a) cross-linked PVP film modified with UV-ozone, (b) PVA film, (c) neat cross-linked PVP film, (d) cross-linked PVP film modified with OTS and (e) CYTOP film measured with nanoindentation tests.

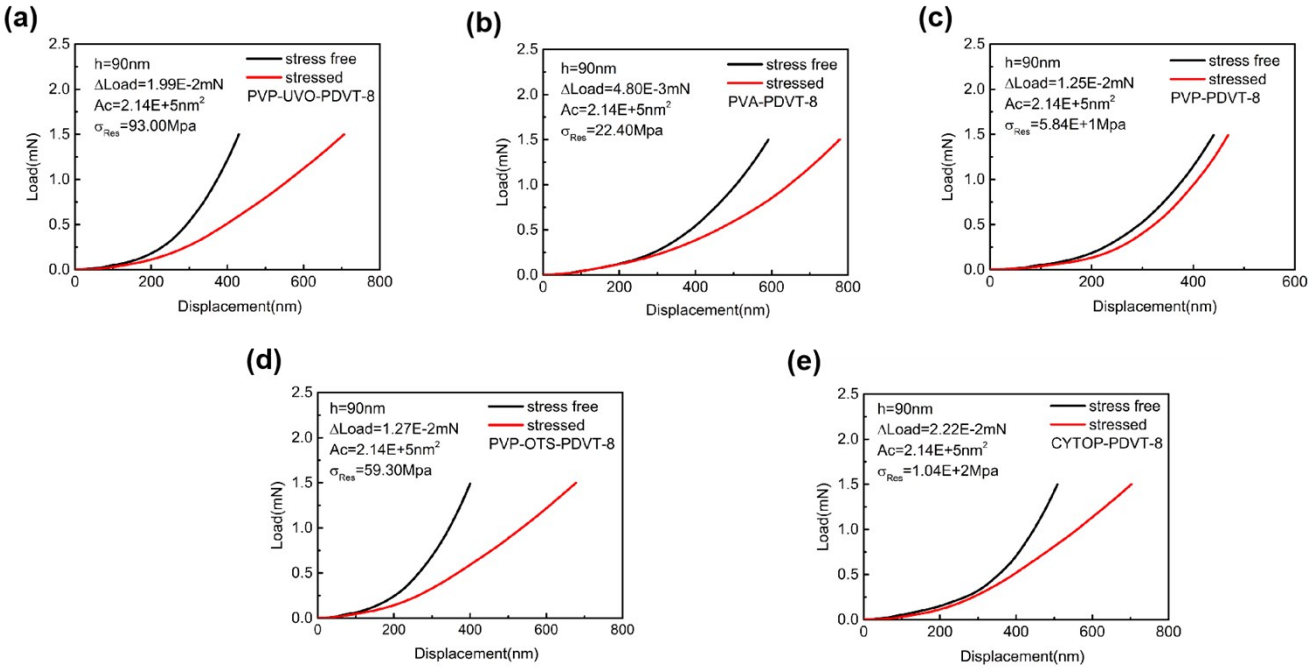

Fig. S4 Load-displacement curves of (a) PDVT-8/PVP-UVO, (b) PDVT-8/PVA, (c) PDVT-8/PVP. (d) PDVT-8/PVP-OTS and (e) PDVT-8/CYTOP bilayer measured with nanoindentation tests.

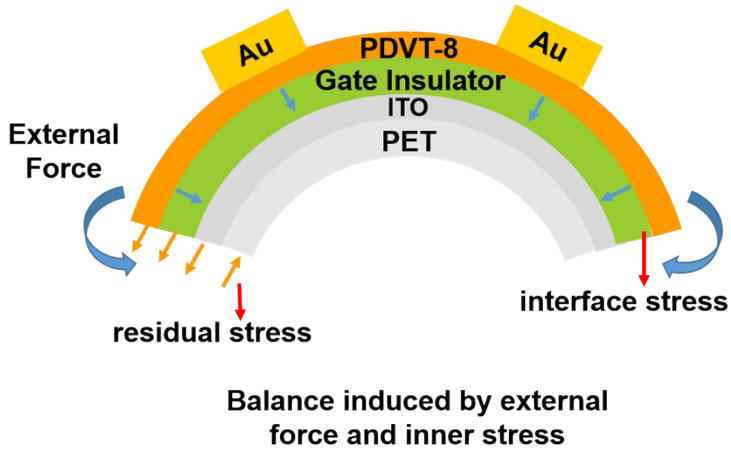

Fig. S5 A schematic of force analysis (including interface stress) of the bending device.

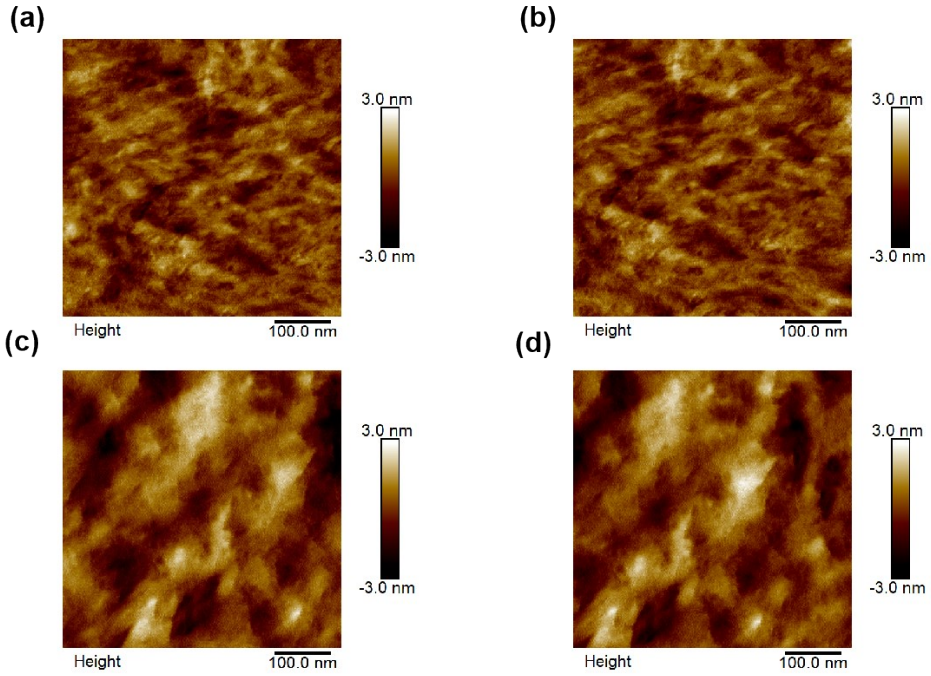

Fig. S6 AFM tapping mode semiconductor morphology of (a) PVP-UVO device without bending test, (b) PVP-UVO device after bending test with bending radius of 5 mm, (c) CYTOP device without bending test, (d) CYTOP device after bending test with bending radius of 5 mm.

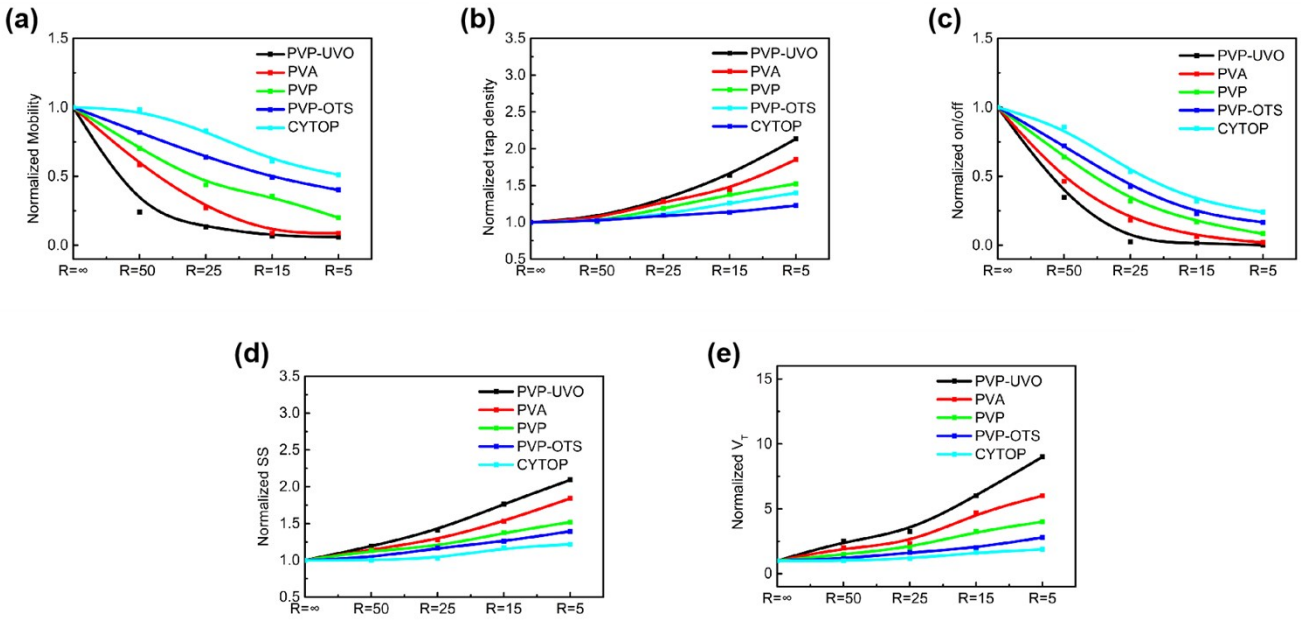

Fig. S7 The curves of flexible OFETs with (a) normalized field-effect mobility, (b) normalized trap density, (c) normalized current on/off ratio, (d) normalized sub-threshold swing (SS) and (e) threshold voltage as a function of bending radius.

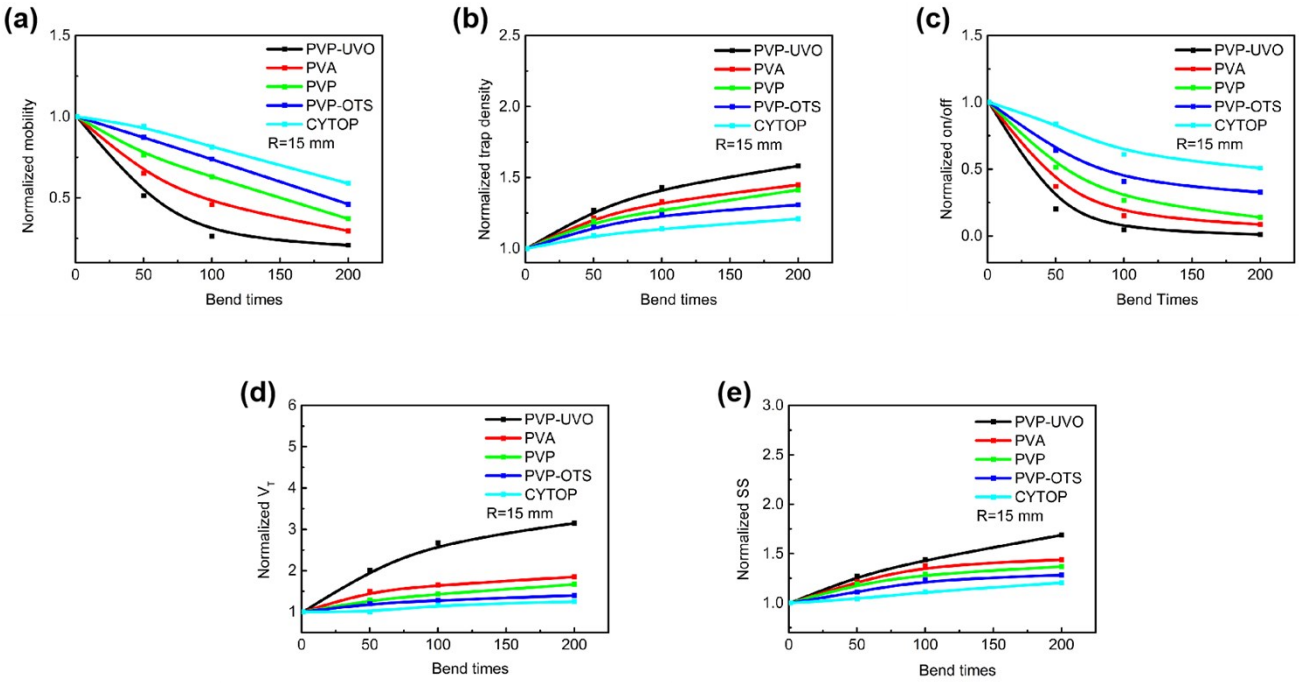

Fig. S8 The curves of flexible OFETs with (a) normalized field-effect mobility, (b) normalized trap density, (c) normalized current on/off ratio, (d) normalized threshold voltage and (e) sub-threshold swing (SS) as a function of bending cycles.

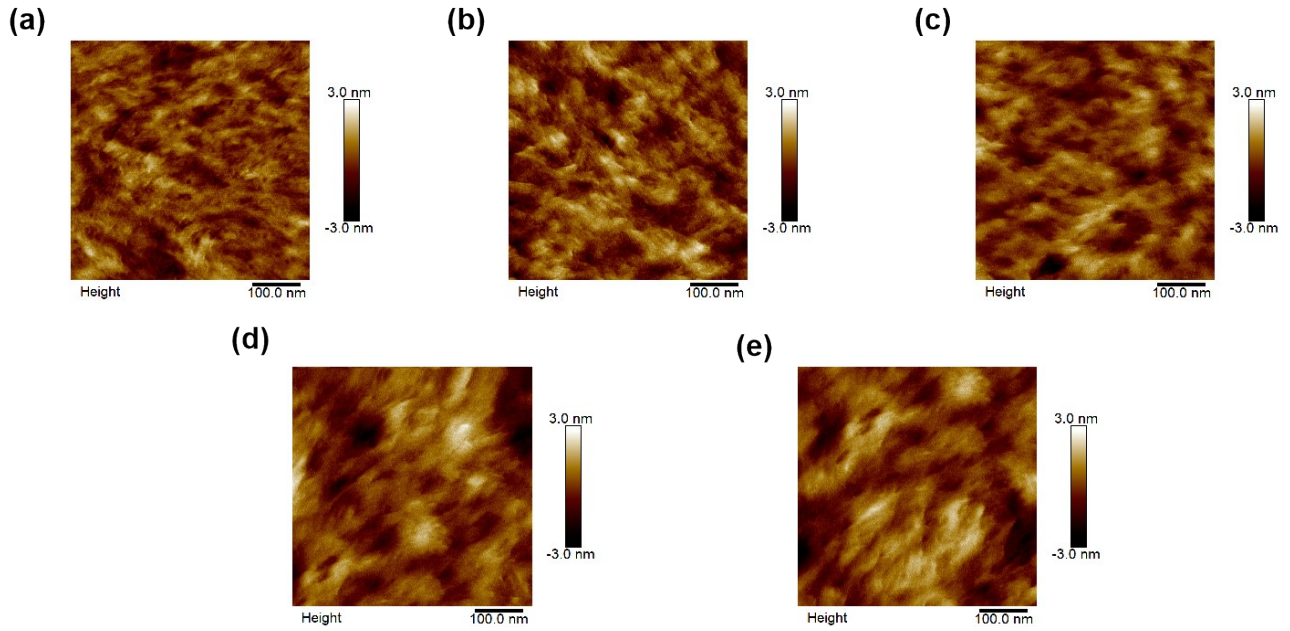

Fig. S9 AFM tapping mode semiconductor morphology of (a) PVP-UVO device, (b) PVA device, (c) PVP device, (d) PVP-OTS device and (e) CYTOP device.

Table S1. The adhesion energy calculated from the surface energy based on the contact-angle measurements

Film	*H_2O(°)*	*CH_2I_2(°)*	*Surface energy(mN/m)*	*Adhesion energy(mN/m)*
PVP-UVO	7.07 ± 4	33.81±3	72.75±0.90	76.75±2.20
PVA	60.44±2	30.43±3	49.75±0.75	75.42±1.42
PVP	75.02±3	31.77±2	44.52±0.83	72.85±1.73
PVP-OTS	52.58±2	103.4±1	33.95±0.50	64.99 ±1.30
CYTOP	112.63±2	83.34±2	20.05±0.60	49.23±1.40
PDVT-8	100.54±4	60.51±3	31.16±1.02	

Supplementary References

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