Electronic Supplementary Information

Solution processed high performance pentacene thin-film transistor

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Contents

1. Experimental Methods

a. Synthesis

Diethyl 6,13-dihydro-6,13-(epoxymethano)pentacene-15,15-dicarboxylate (**1**): To a slurry of pentacene (500 mg, 1.8 mmol) in toluene (15 ml) was added diethyl ketomalonate (2.8 ml, 18.4 mmol) with stirring. The dark blue solution was heated to reflux, while the color was slowly turned to yellow. After 24 hours, the reaction mixture was evaporated under reduced pressure to remove solvent, and then the residue was purified by silica gel column chromatograph eluent with ethyl acetate/n-hexane (1/3). Compound **1** was obtained in 60% yield (488 mg). Physical data of **1**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.81~7.86 (m, 8H), 7.46~7.48 (m, 4H), 6.25 (s, 1H), 5.36 (s, 1H), 3.98 (q, J = 7.0 Hz, 4H), 1.02 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 168.23, 138.49, 134.99, 133.38, 133.04, 128.63, 128.30, 126.96, 126.79, 124.73, 122.51, 83.25, 77.09, 62.51, 49.18, 14.21; IR (KBr): 2975, 1744, 1635, 1285, 1235, 1092, 1056, 955, 754 cm^{-1}.

b. OTFTs Fabrication and Measurements

Thin-film transistors were fabricated on a heavily n-doped silicon substrate with a silicon dioxide layer (300 nm) in top contact geometry. The substrates were cleaned by freshly prepared piranha solution for 3 hours and then washed with de-ionized water, and dried with nitrogen gas. The piranha-cleaned water was placed in an environment saturated with hexamethyldisiloxane (HMDS) for 24 hours, followed by rinsing in toluene. Compound **1** was dissolved in chloroform (50 mg/ml) and spin-coated on the wafer (spin rate 550 rpm for 75 seconds). It was then heated to 210 ^{o}C for 7 minutes, and then cooled down to room temperature. The procedure was repeated for six times, while a smooth film can be obtained. The thickness of pentacene films was estimated to be in a range of 1.6~1.9 μm, averaged from 20 independent pieces which were measured by a Veeco Dektak 150 Surface Profilometer. A layer of gold (100 nm) was thermally deposited at a rate 0.1 nm s^{-1} under a reduced presure (5 x 10^{-6} torr) though a shadow mask with W/L of 10 (W = 500 μm, L = 50 μm). The electrical measurements were carried out in air using a semiconductor parameter analyzer (Keithley 2636).

2. ^{1}H and ^{13}C NMR spectra

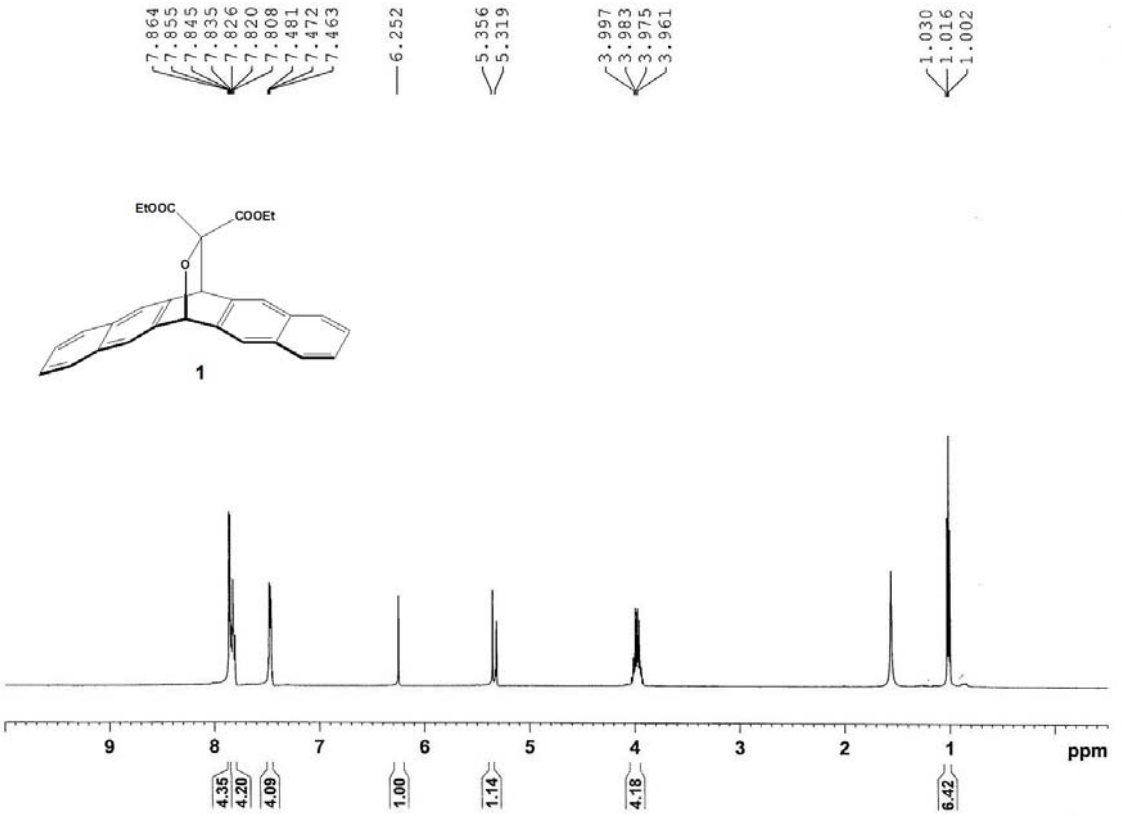


Figure S1. ^{1}H NMR of **1**.

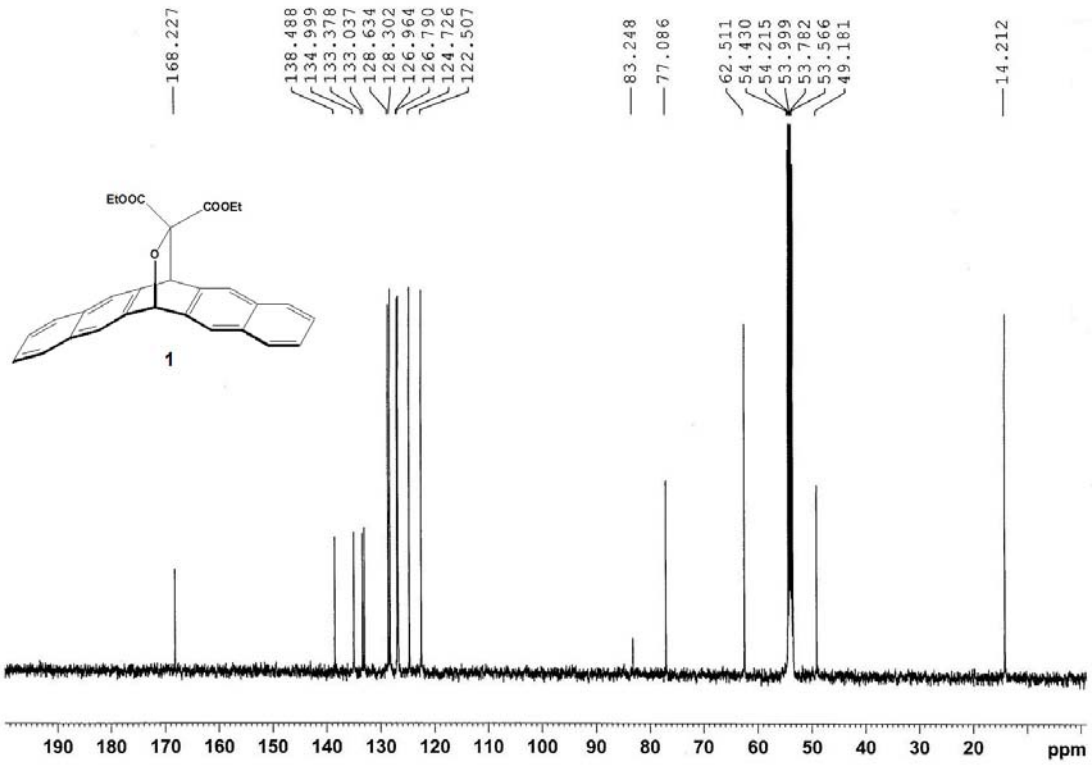


Figure S2. ^{13}C NMR of **1**.

IR spectra

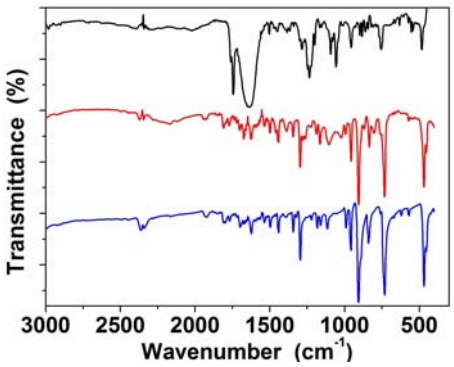


Figure S3. Infrared spectra of compound **1** before (black line) and after (red line) heating at 210 °C for 30 min. A standard infrared spectrum of commercial pentacene (blue line) is presented at the bottom for comparison.

4. SiO_2/Si substrate lithographically patterned with gold, and that is used in the experiments

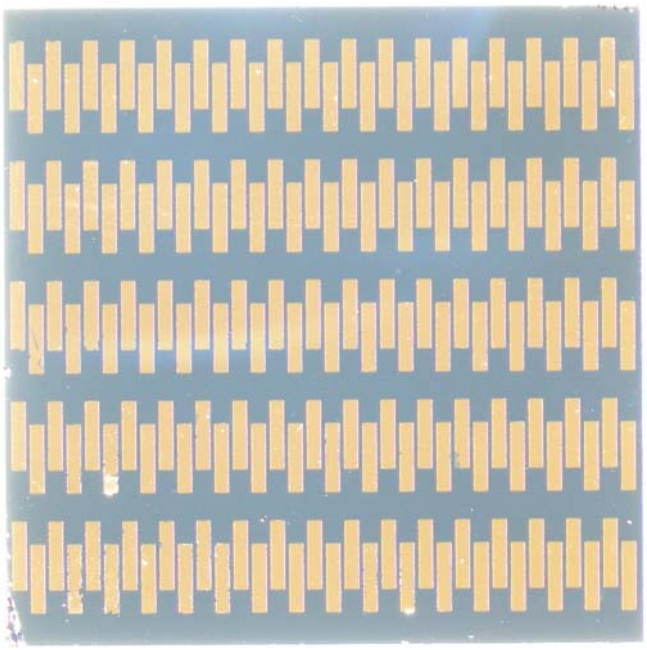


Figure S4. SiO_2/Si substrate lithographically patterned with gold, showing the coverage of gold on the surface of SiO_2. The dimension of the wafer is 7 mm x 7 mm, for each electrode (170 pieces) is 0.75 mm x 0.15 mm, and for each channel is 500 μm x 50 μm. For the measurement of WAXRD, the beam size was 12 × 0.4 mm.

5. XRD plots

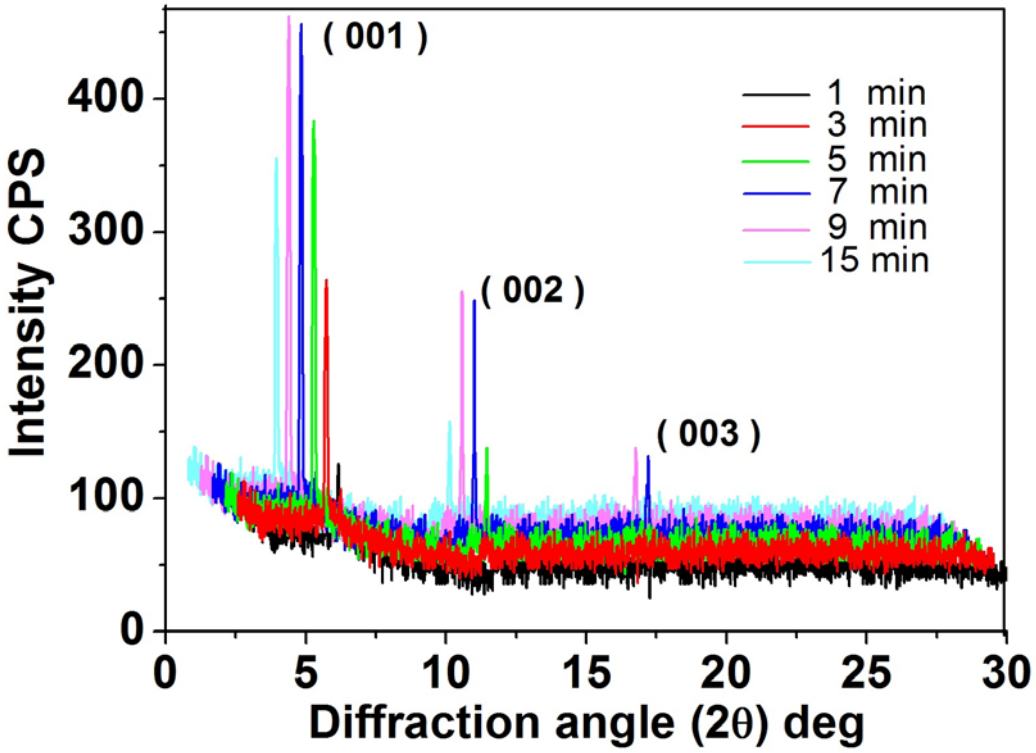


Figure S5. Out-of-plane wide-angle X-ray diffraction patterns of device 1 with different time scale at 210 ^{o}C. The six colour lines in a group are shifted slightly for better illustration, but they are actually appeared at the position identical to the black line (1 min).

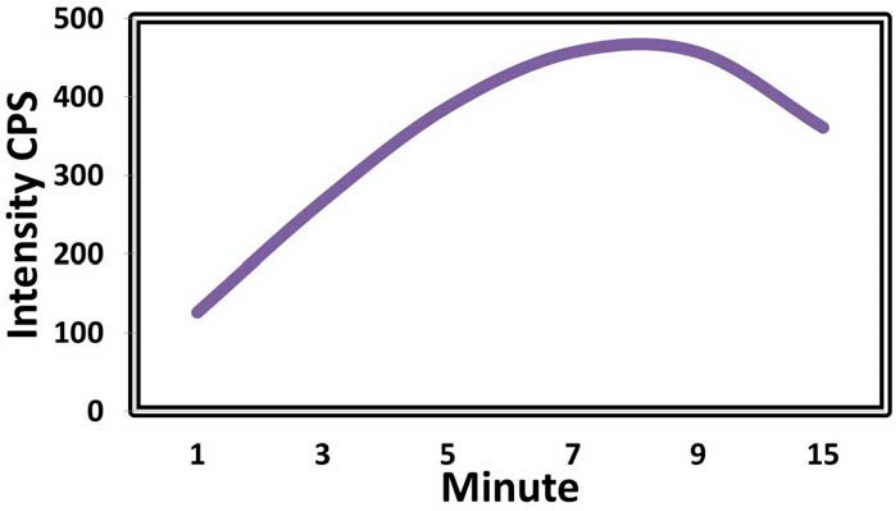
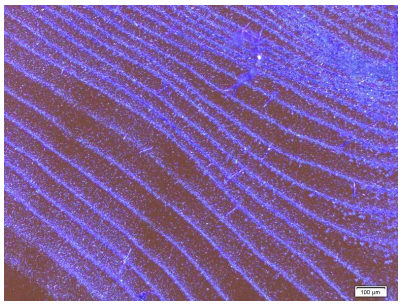
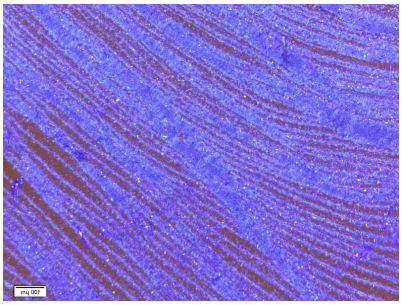


Figure S6. Out-of-plane wide-angle X-ray diffraction patterns of device 1 pentacene (001) intensity with different time scale at 210 ^{o}C.

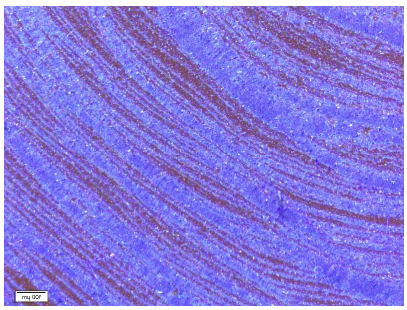
6. Film morphology



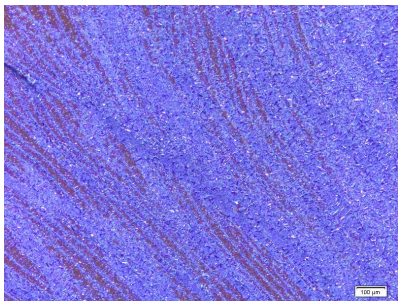
1st spin-then-heat



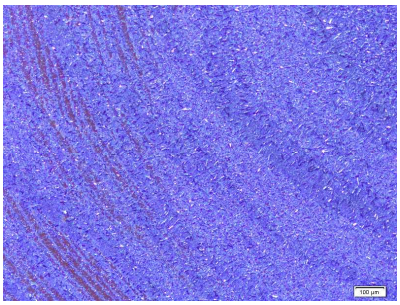
2nd spin-then-heat



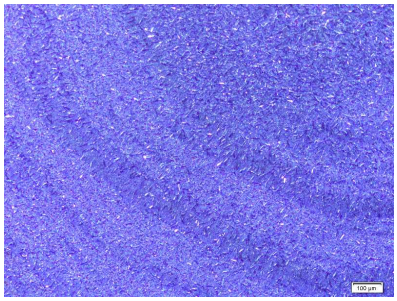
3rd spin-then-heat



4th spin-then-heat

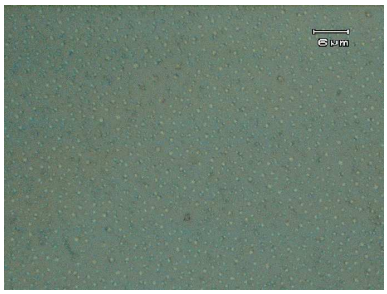


5th spin-then-heat

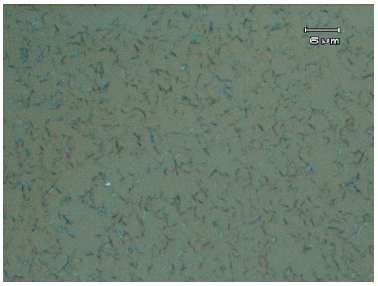


6th spin-then-heat

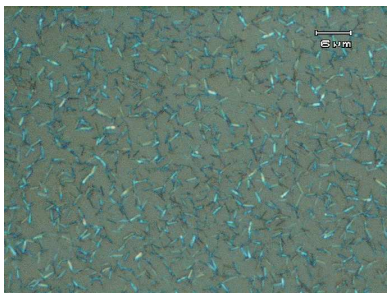
Figure S7. Microscopic images of surface morphology during the multiple spin-then-heat treatment of compound **1**, showing that pentacene is filling into the gaps left by the previous step.



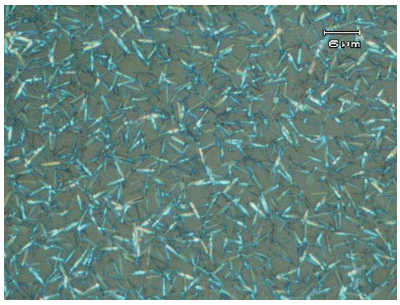
1st spin-coating without heating



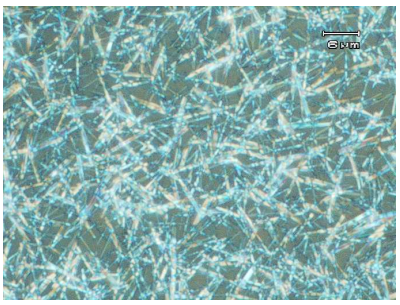
2nd spin-coating without heating



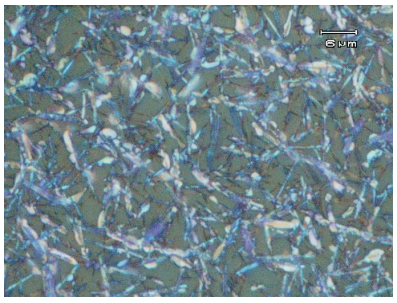
3rd spin-coating without heating



5th spin-coating without heating

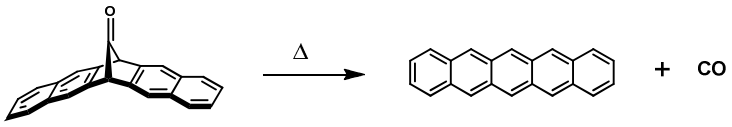


10th spin-coating without heating

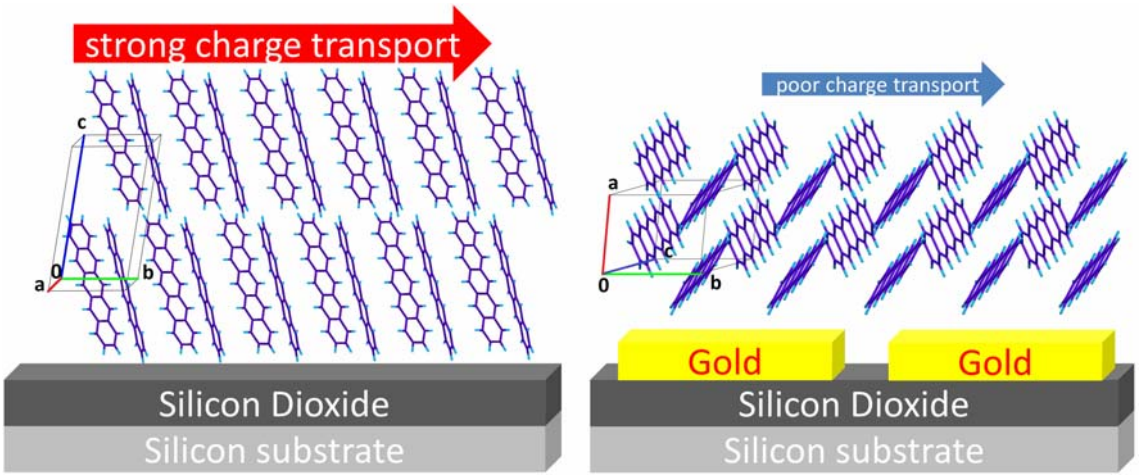


heated after 10th spin-coating

Figure S8. Microscopic images of surface morphology after multiple spin-coating of an analogous precursor (below), showing the formation of web-like structure with pinholes (for comparison).



7. Crystal alignments



Top-contact (TC) design **Bottom-contact (BC) design**

Figure S9. In a TC design, a pentacene film was deposited directly on the surface of SiO_2, while strong signals corresponding to (001), (002), and (003) diffraction angles were detected. The *d* spacing of 15.4 A indicated that pentacene molecules were aligned with their long axis parallel to the surface normal (left). However in a BC design, a pentacene film was deposited on the SiO_2 lithographically patterned with gold. In the WAXRD spectrum, it displayed a strong peak at 28.28°, corresponding to a *d* spacing of 3.15 A. It implies that pentacene molecules were lying down on the surface with the *a* axis standing vertically on the surface (right). In a BC design the gold metal underneath the pentacene film did interfere the packing pattern of pentacene.

8. OFET characteristics

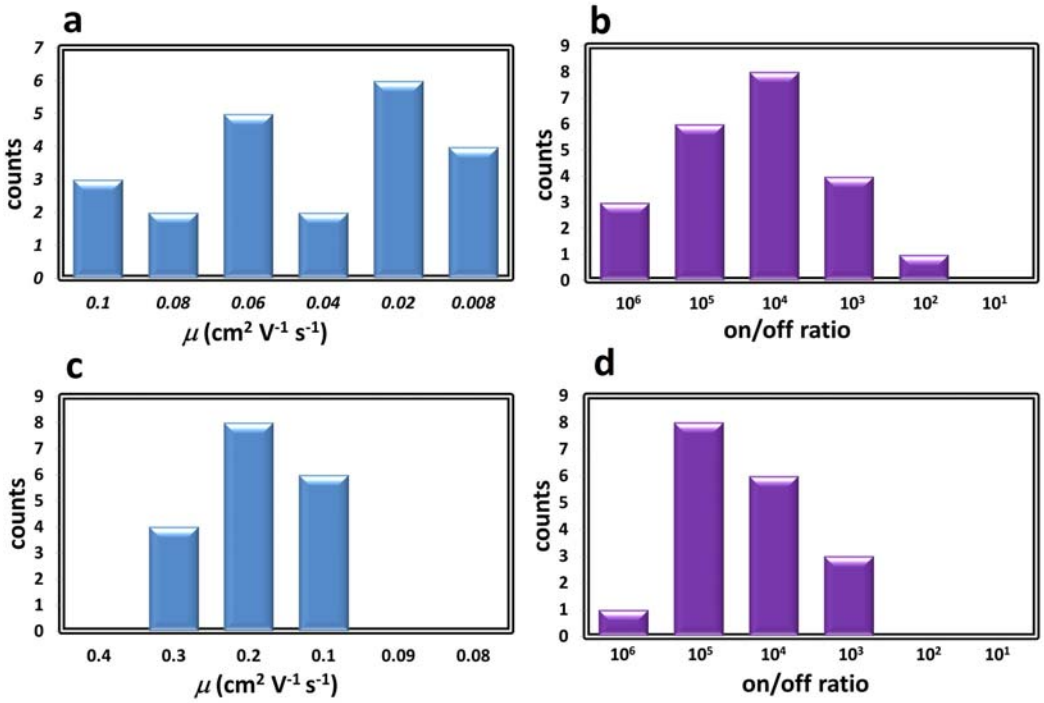


Figure S10. Performance of measured spin-coated top-contact OTFT devices; in histogram: upper; device 1 without surface treatment on bare SiO_2 (a) FET mobility and (b) on/off ratio, under; device 2 surface treatment with Hexamethyldisiloxane HMDS (c) FET mobility and (d) on/off ratio.

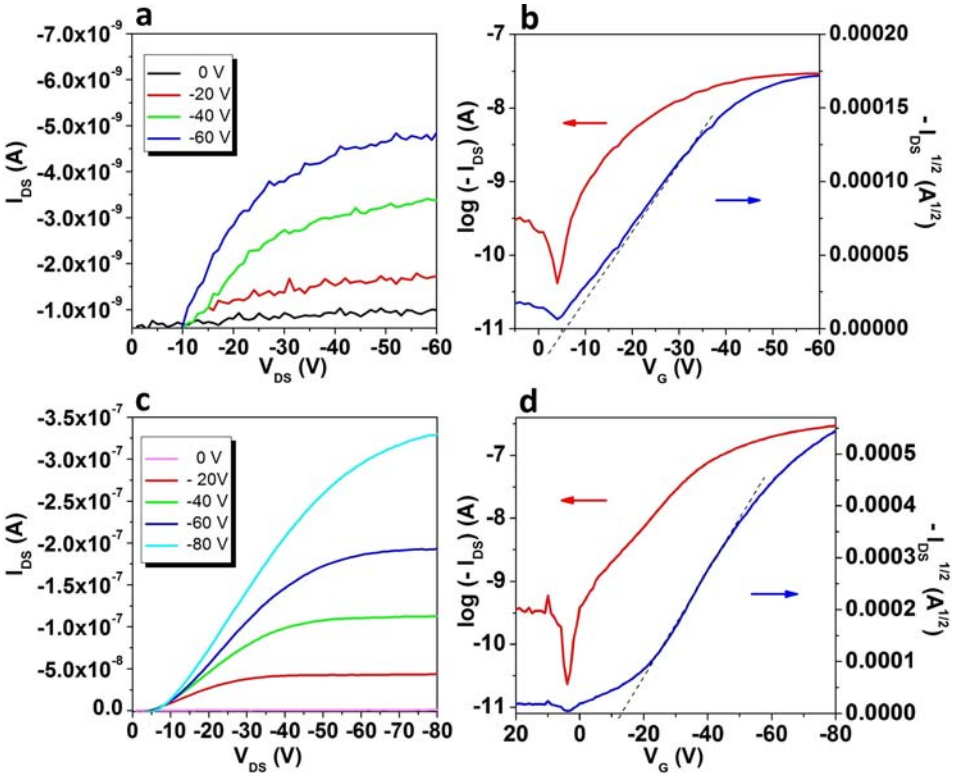


Figure S11. (a) Typical output and (b) transfer characteristics of device 3; (c) typical output and (d) transfer characteristics of device 4 (channel width of 500 μm and a channel length of 50 μm, and $I_{DS}^{1/2}$ vs. V_G in the saturation mode).

9. AFM images

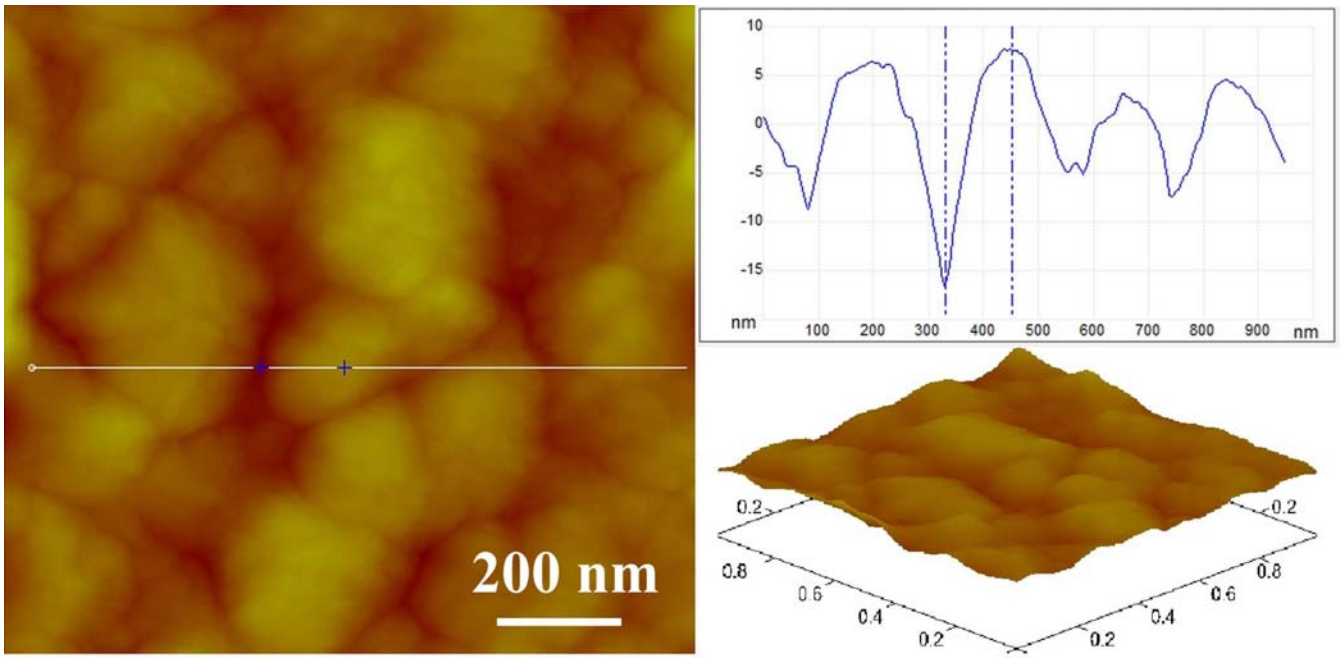


Figure S12. AFM topographic images of precursor **1** thin film on SiO_2, roughness: 20 nm, z scale: 100 nm.

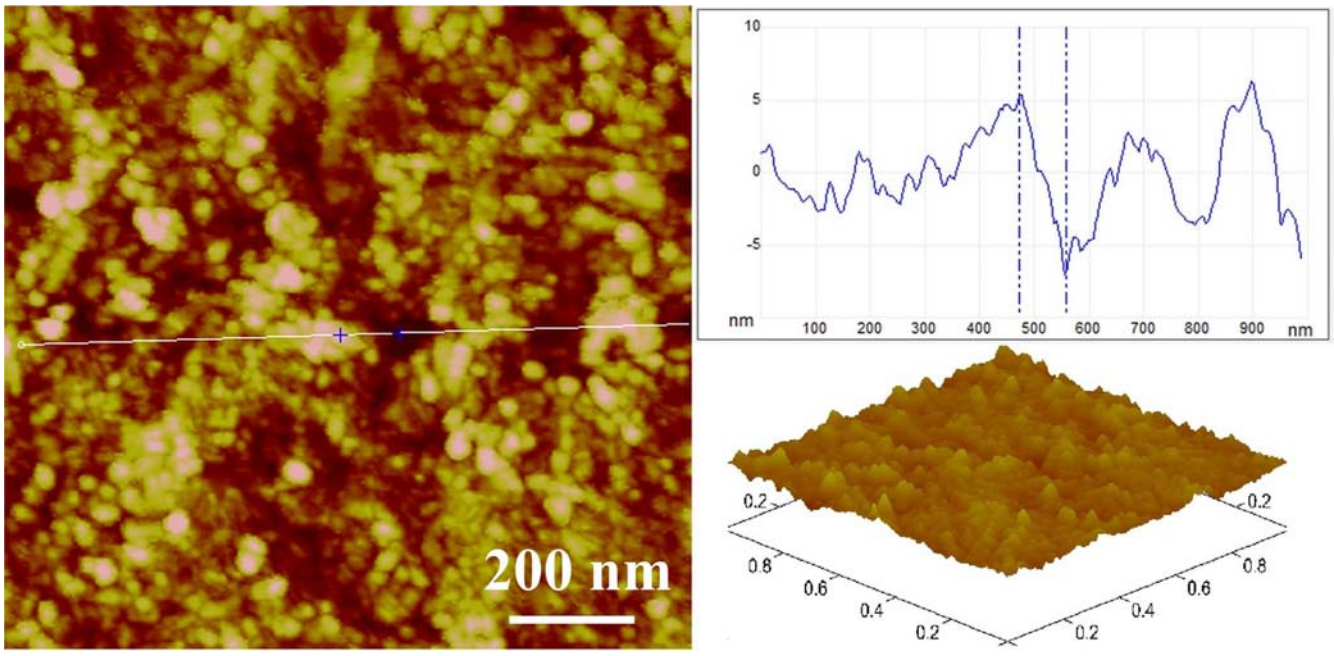


Figure S13. AFM topographic images of pentacene (200) converted from precursor **1** thin film on bare gold surface, roughness: 11 nm, z scale: 10 nm.

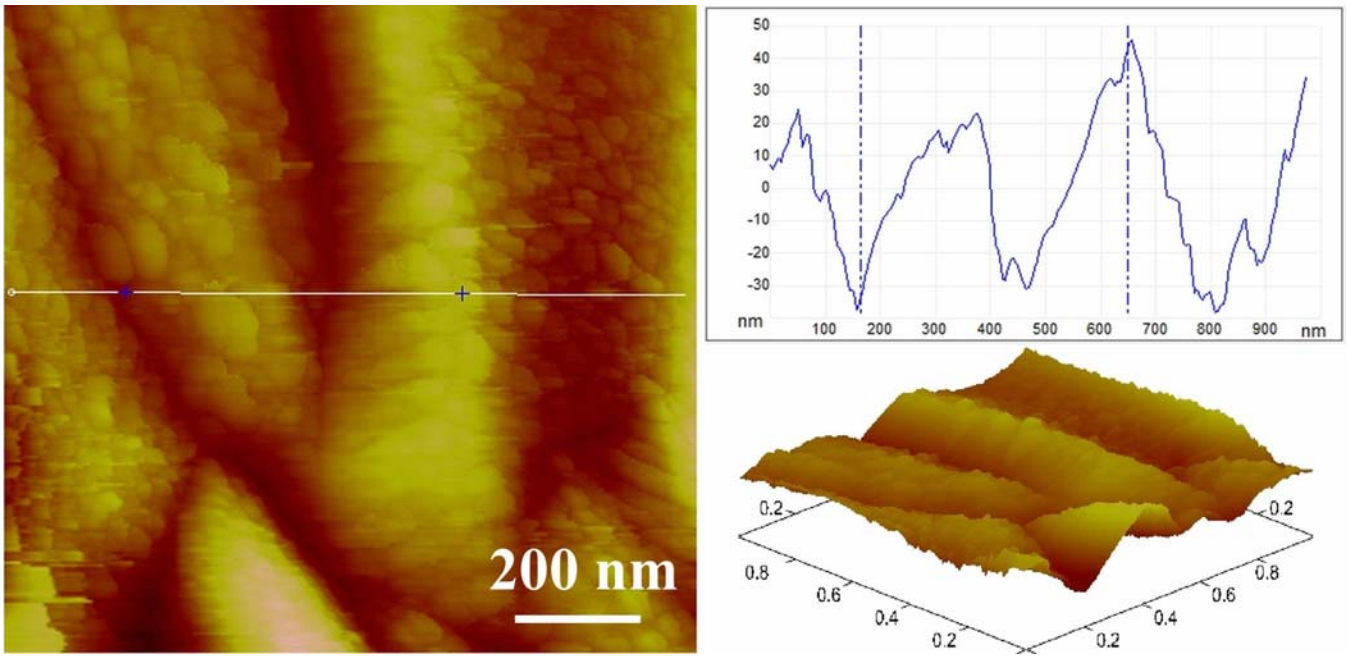


Figure S14. AFM topographic images of pentacene converted from precursor **1** thin film on bare SiO_2 surface (device 1), roughness: 70 nm, z scale: 500 nm.

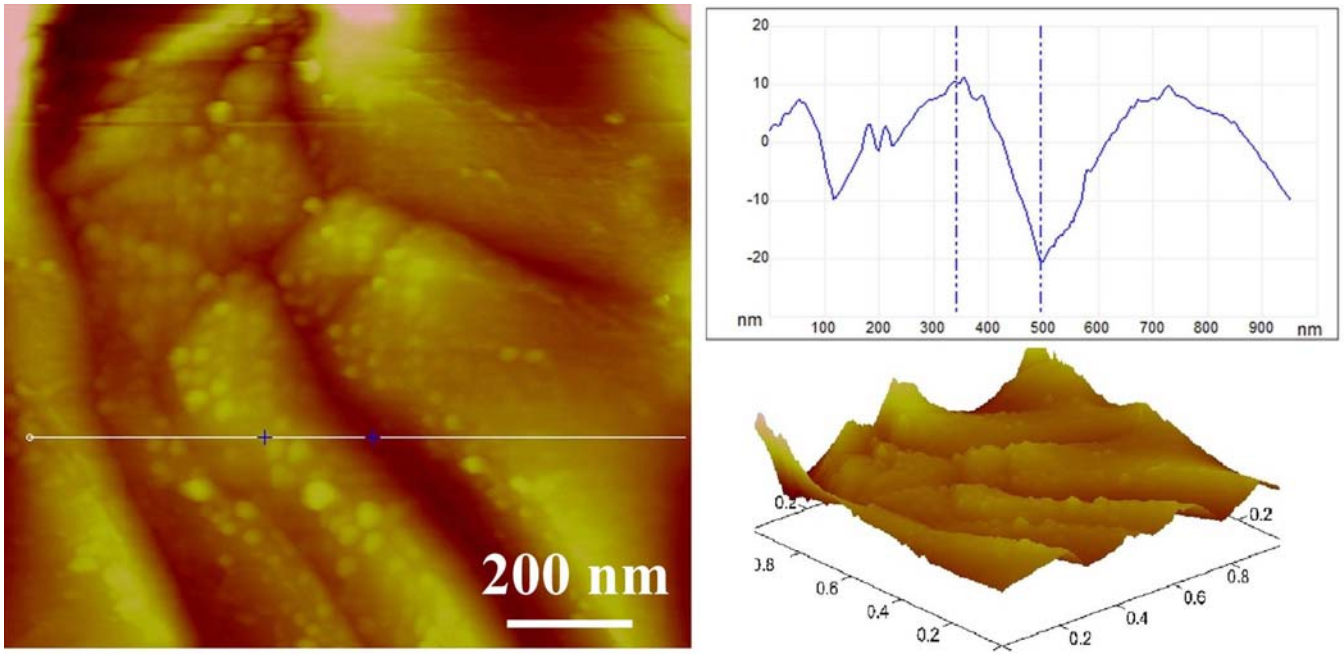


Figure S15. AFM topographic images of pentacene converted from precursor **1** thin film on $HMDS/SiO_2$ surface (device 2), roughness: 30 nm, z scale: 200 nm.

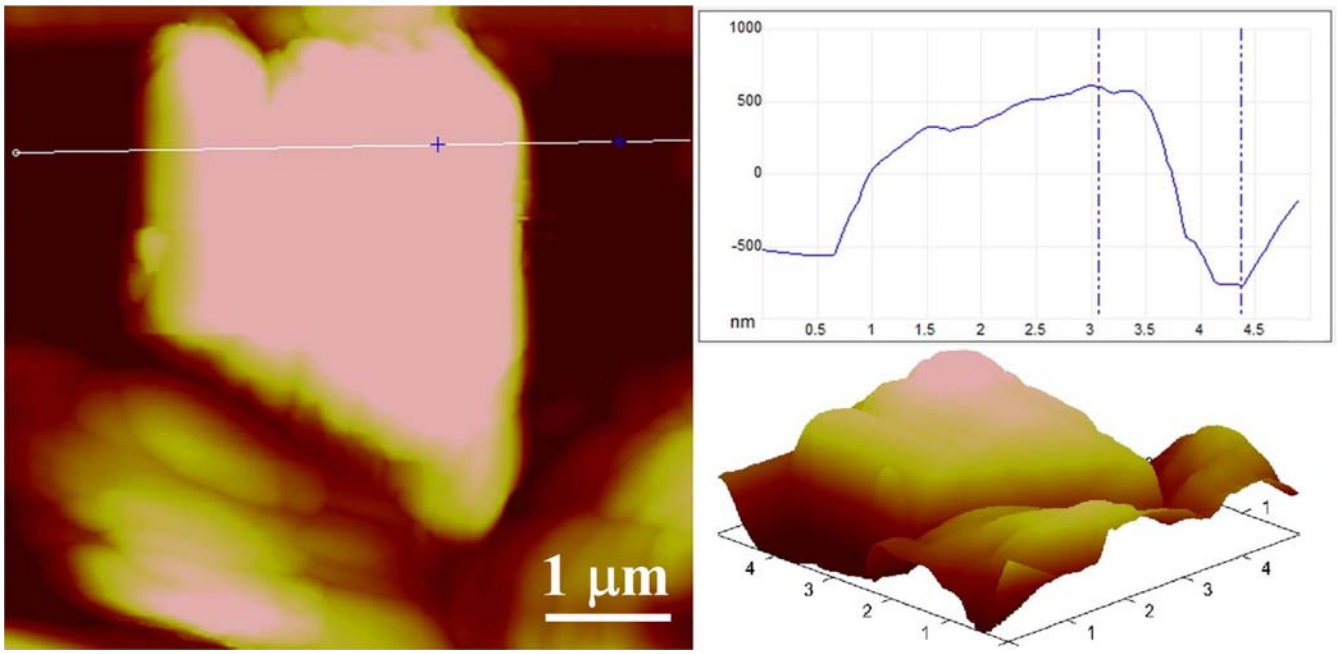


Figure S16. AFM topographic images of pentacene converted from precursor **1** thin film on SiO_2 surface (device 3), roughness: 1367 nm, z scale: 500 nm.

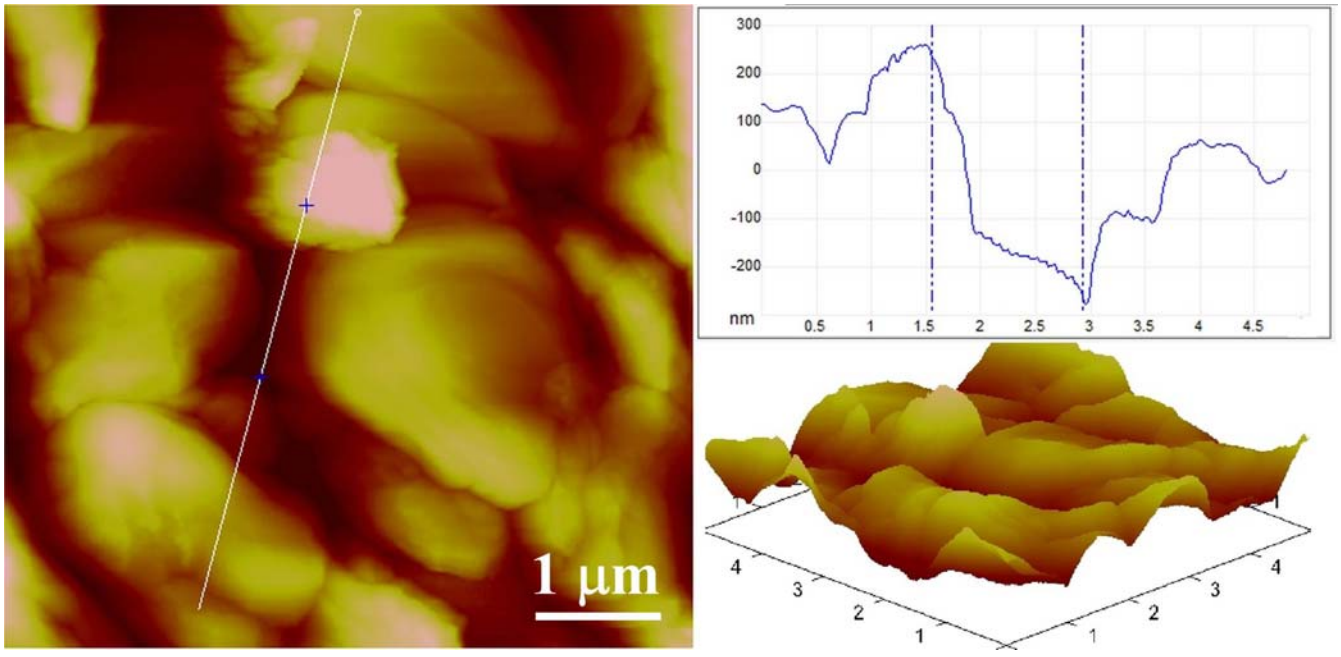


Figure S17. AFM topographic images of pentacene converted from precursor **1** thin film on HMDS/SiO_2 surface (device 4), roughness: 514 nm, z scale: 500 nm.