Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
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Electronic Supplementary Information for:

Induced Crystallization of Rubrene with Diazapentacene as the Template

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1. Materials

Rubrene was purchased from International Laboratory USA, and purified with a physical vapor transport system[1] prior to device fabrication. Octadecyltrimethoxysilane (OTMS) and octadecylphosphonic acid (ODPA) were purchased from Aldrich and International Laboratory USA respectively, and were both used without purification. 6,13-diazapentacene (DAP) was prepared by oxidizing 6,13-dihydro-6,13-diazapentacene [2] following the reported method [3] and purified with a physical vapor transport system prior to device fabrication.

2. Cyclic voltammetry

The cyclic voltammetry of DAP was performed in a saturated solution in anhydrous DMF with 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte, at a scan rate of 50mV/s. A platinum bead was used as a working electrode, with a platinum wire as an auxiliary electrode and a silver wire was used as a pseudo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus $FeCp_2^+/FeCp_2^0$.

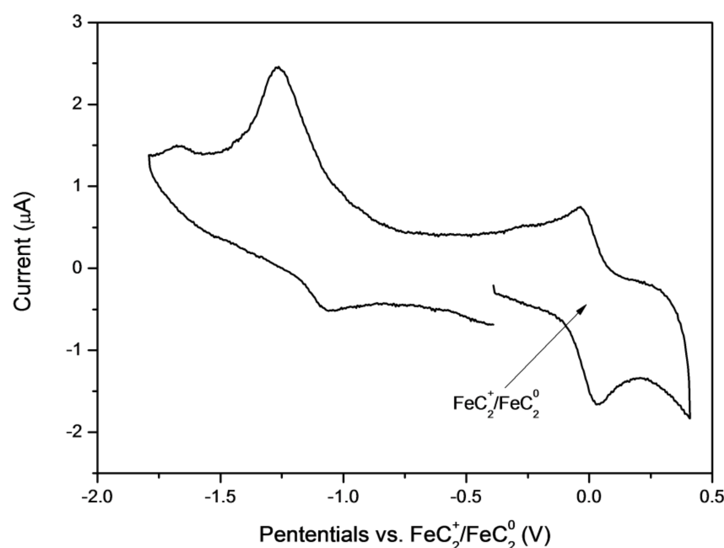

Figure S-1 Cyclic voltammogram of DAP recorded in DMF with $FeCp_2^+/FeCp_2^0$ as the internal standard.

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1. R. A. Laudise, C. Kloc, P. G. Simpkins, T. Siegrist, *J. Cryst. Growth* **1998**, 187, 449.
2. Q. Miao, T.-Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 10284.
3. J. A. VanAllan, R. E. Adel, G. A, Reynolds, *J. Org. Chem.* **1962**, *27*, 2873.

3. UV-vis absorption spectroscopy

UV-vis absorption spectra were recorded on a Varian CARY 1E UV-vis spectrophotometer. The 40nm-thick thin film of DAP for UV-vis absorption spectroscopy was deposited on a quartz wafer.

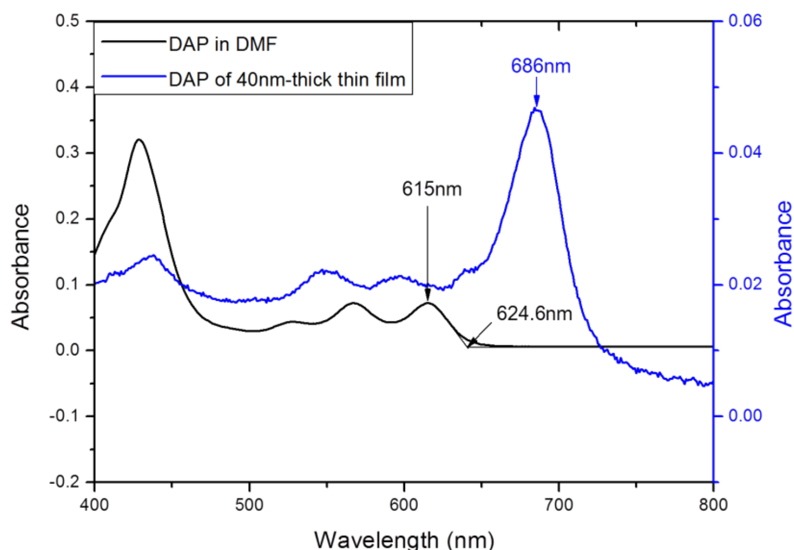

Figure S-2 Absorbance spectra of DAP in DMF at a concentration of 1×10^{-5} mol/L and in 40nm-thick thin film.

Table S-1 Reduction, absorption edge and estimated frontier molecular orbital energy levels of DAP

$E_{red}^{1/2}$ vs. Fc^{+}/Fc	Absorption edge	Optical gap	LUMO [a]	HOMO [b]
-1.17V	624.6 nm	1.93eV	-3.63eV	-5.56eV

[a] Estimated from $E_{LUMO} = -4.80 - E_{red}$ (eV) [4]. [b] Calculated from E_{LUMO} = Gap + E_{HOMO}

4. Deposition of thin films and fabrication of thin film transistors

Thin films for UV-vis absorption were deposited on quartz plates and thin films for other experiments were deposited on silicon wafers, which had 300 nm-thick SiO_2 on highly n-doped Si. The SiO_2 surface was modified with octadecylphosphonic acid (ODPA) [5] or octadecyltrimethoxysilane (OTMS) [6] as needed by following the reported procedures. All thin films were vacuum-deposited by an Edward Auto 306 vacuum coating system with a Turbomolecular pump at a pressure of 2.0×10^{-6} torr or lower, with a deposition rate of ca. 2 nm/min to desired thickness as measured by a quartz crystal sensor. DAP was chemically

4. The commonly used HOMO energy level of ferrocene is −4.80 eV. See: a) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, *7*, 551; b) B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov, M. E. Thompson, *Org. Electron.* **2005**, *6*, 11.
5. Z. Li, J. Du, Q. Tang, F. Wang, J. Xu, J. C. Yu, Q. Miao, *Adv. Mater.* **2010**, *22*, 3242.
6. Y. Ito, A. A. Virkar, S. Mannsfeld, J. H. Oh, M. Toney, A. Locklin, Z. Bao, *J. Am. Chem. Soc.* **2009**, *131*, 9396.

unchanged under the deposition conditions as found by using ^{1}H NMR spectroscopy.[7] During vacuum deposition the distance between source and substrate was 18.5 cm. Substrate temperatures during deposition were achieved using a radiant heater and measured with a thermocouple.

To fabricate organic thin film transistors, top contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films in the same vacuum chamber, and the resulting semiconducting channels were 50μm(L)×1mm(W), 100μm(L)×1mm(W), 50μm(L)×2mm(W) and 100μm(L)×2mm(W). These transistors had highly n-doped silicon functioned as gate electrode and 300 nm-thick SiO_2 as dielectrics.

5. X-ray diffraction (XRD) from thin films

XRD data were recorded on a SmartLab X-Ray Refractometer from the thin films of DAP and rubrene (both ca. 100nm thick) deposited on varied surfaces. (The substrate temperature was kept at 60 ℃ during the deposition of DAP and at 90 ℃ during the deposition of rubrene.)

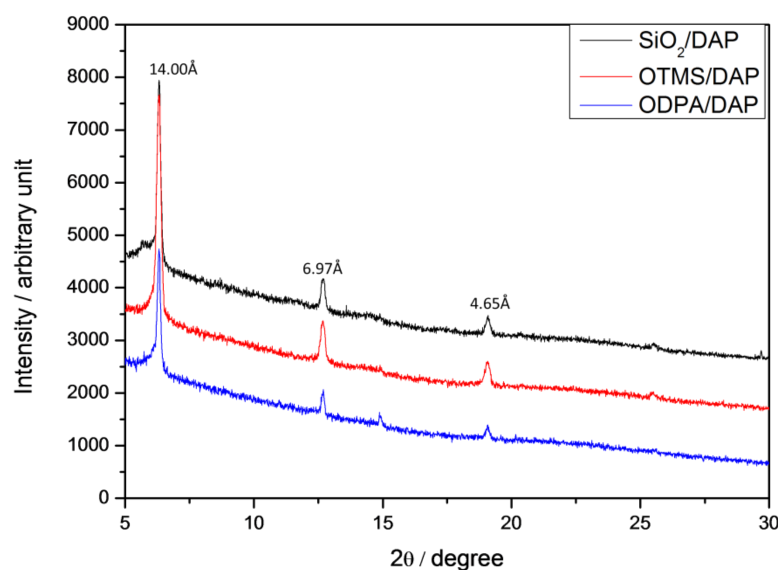

Figure S-3 X-ray diffraction from 100 nm-thick films of DAP deposited on bare SiO_2, OTMS-modified SiO_2 and ODPA-modified SiO_2 at substrate temperature of 60 ℃.

6. Characterization of thin film transistors

The current-voltage measurement of thin-film transistors was conducted in ambient air at room temperature using JANIS ST-500-20-4TX probe station and a Keithley 4200 Semiconductor Characterization System.

7. An 100 nm-thick film of DAP deposited on the bilayer ODPA-modified SiO_2 was dissolved in DMSO-d_6, and only three sets of peaks for DAP were found in the ^{1}H NMR spectrum.

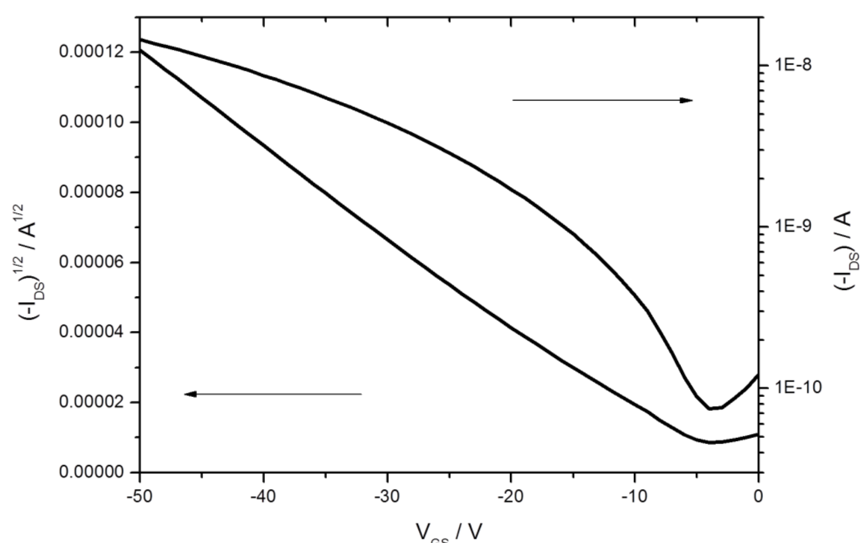

Figure S-4 Drain current (I_{DS}) versus gate voltage (V_{GS}) with V_{DS} = -50V measured in air from the thin film transistors of DAP deposited on ODPA-modified SiO_2 at substrate temperature of 60 ℃ with channel dimension W = 1mm and L = 50μm. This device exhibited hole mobility of 6×10^{-5}cm^2/V·s as measured from the saturation regime.

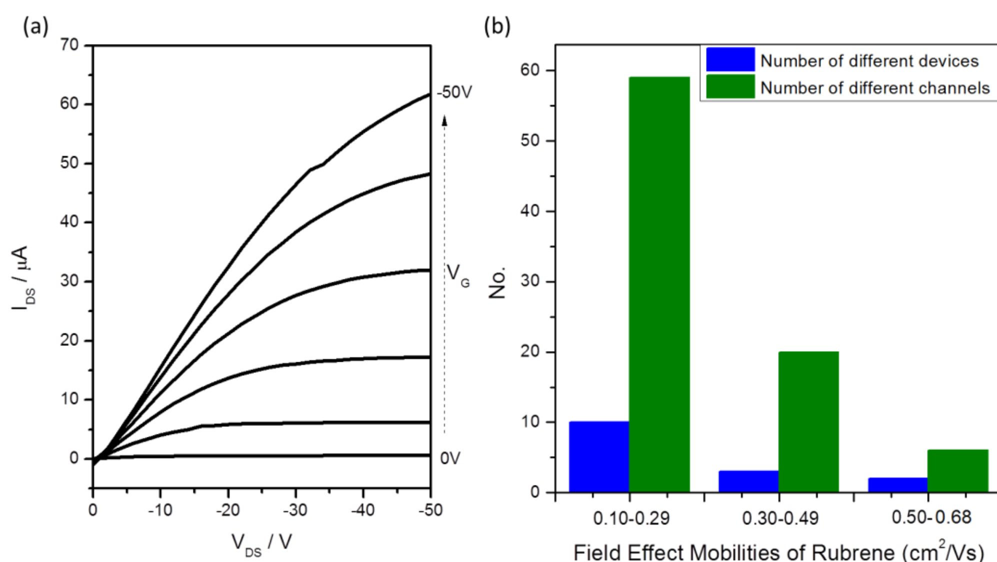

Figure S-5 (a) Drain current (I_{DS}) versus drain voltage (V_{DS}) with varying gated voltage (V_{GS}, from 0 to −50 V in −10 V steps) for organic thin film transistors of rubrene deposited on ODAP--modified SiO_2 at substrate temperature of 90 ℃ with channel dimension of W = 1 mm and L = 50 μm and (b) Summary of thin film transistor performance of rubrene deposited under high vacuum at room temperature.

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7. Atomic force microscopy (AFM) study

Thin films of DAP (ca. 100nm thick) deposited at 60 ℃ on bared SiO_2, OTMS-modified SiO_2 and ODPA-modified SiO_2 were used for AFM studies. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments. All AFM images were collected using tapping mode and in air under ambient conditions. The topographic images were collected from multiple samples, and for each sample, different regions were scanned to ensure reproducibility.

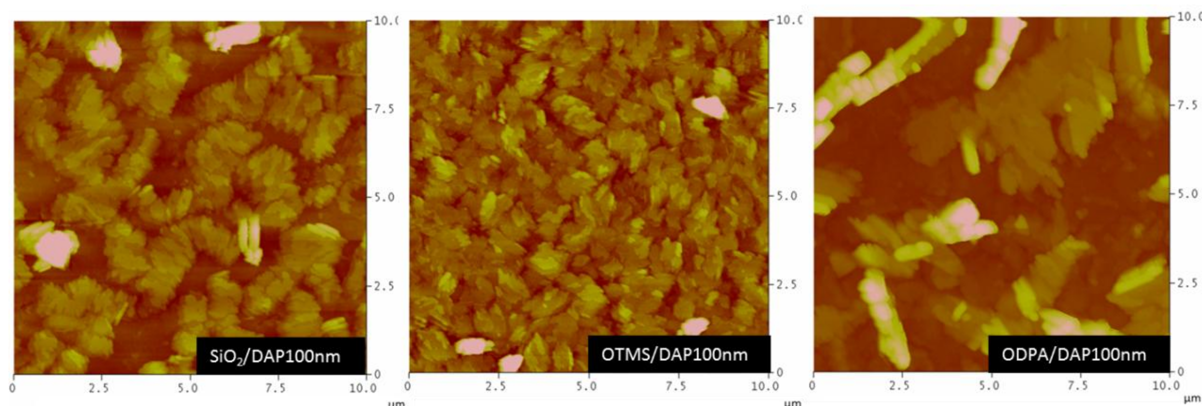

Figure S-6 AFM height images of thin films of DAP (ca. 100nm thick) deposited on bare SiO_2, OTMS-modified SiO_2 and ODPA-modified SiO_2.

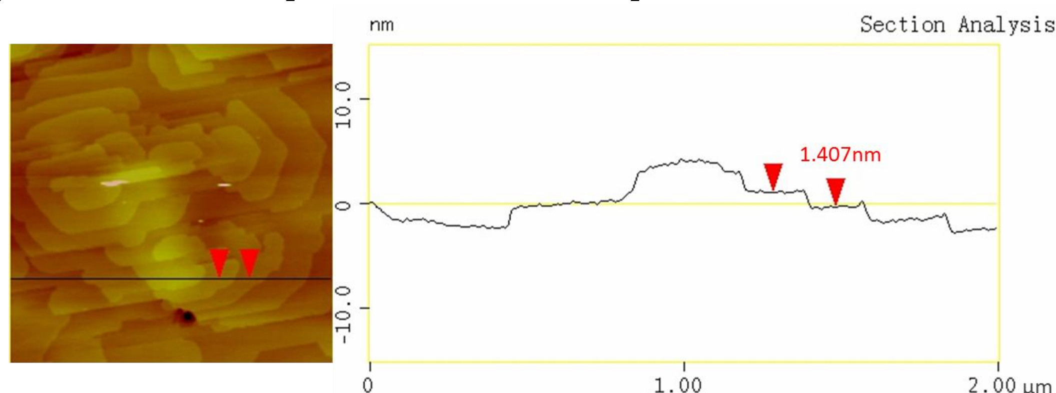

Figure S-7 AFM height image and section analysis of the crystal surface of rubrene film, which was deposited on ODPA-modified SiO_2, showing terrace height of about 1.4 nm.

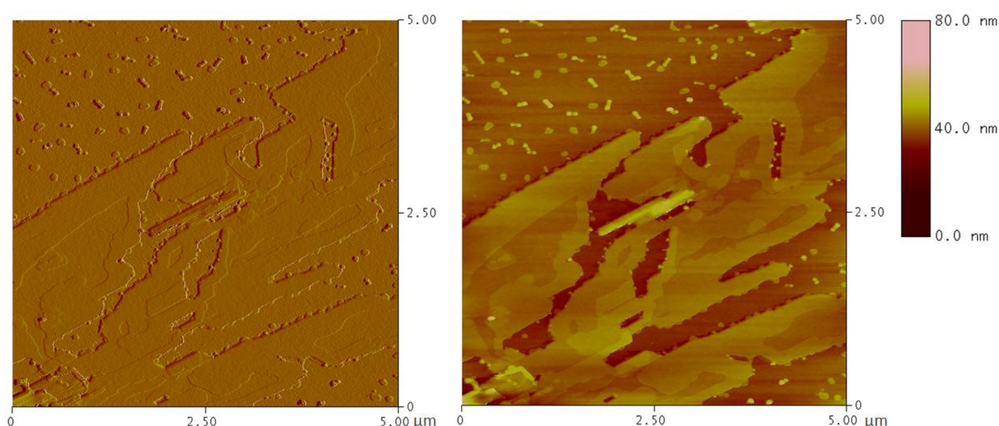

Figure S-8 AFM amplitude (left) and height (right) images for a film containing 3 nm-thick rubrene deposited on 3 nm-thick DAP on ODPA bilayer-step surface. (Rubrene only covered part of the surface and the AFM images were taken from an area covered by rubrene.)

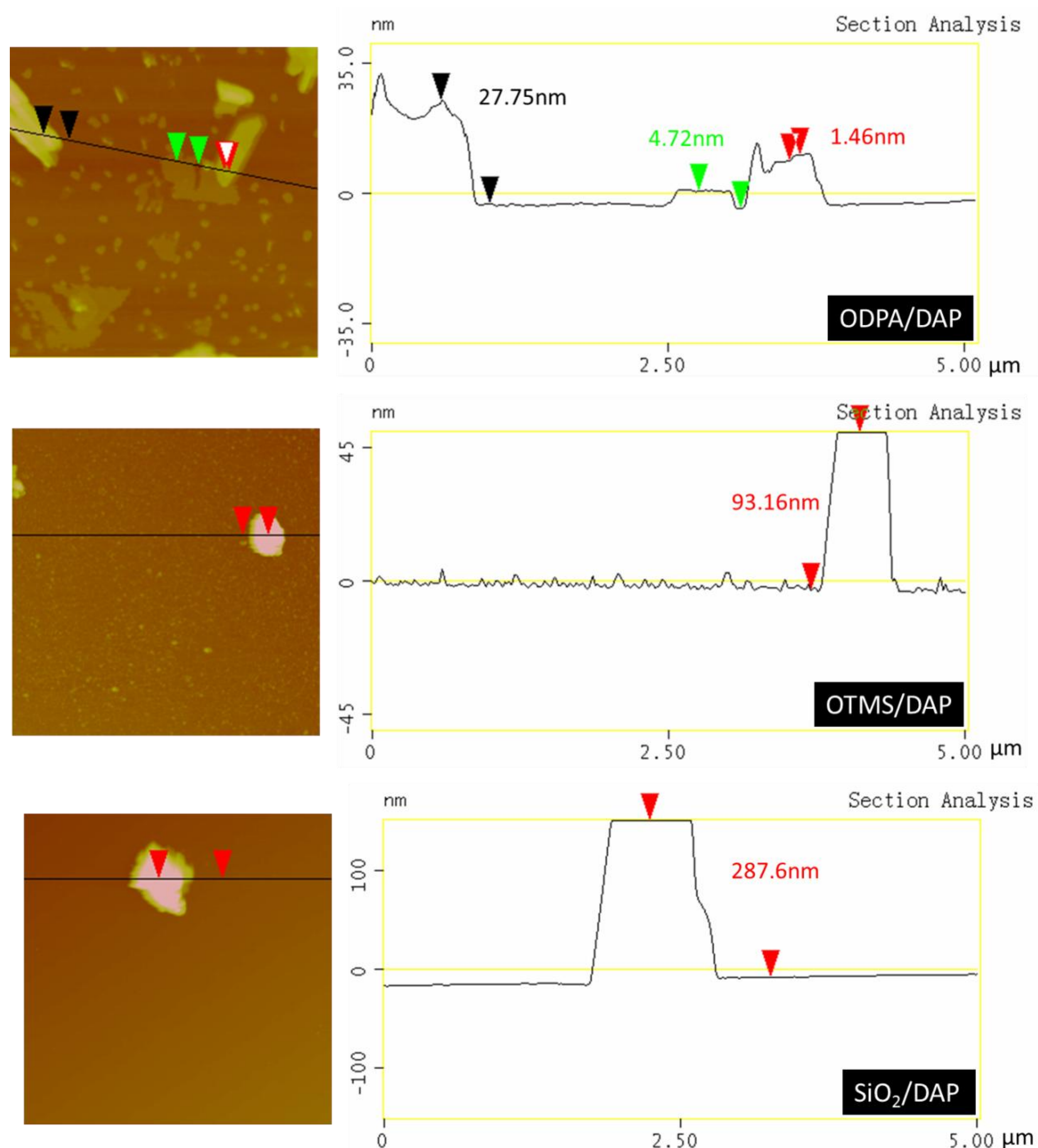

Figure S-9 AFM section analysis for films of DAP with the norminal thickness of 3 nm deposited on the surfaces of (a) ODPA-modified SiO_2, (b) OTMS-modified SiO_2, (c) bare SiO_2.

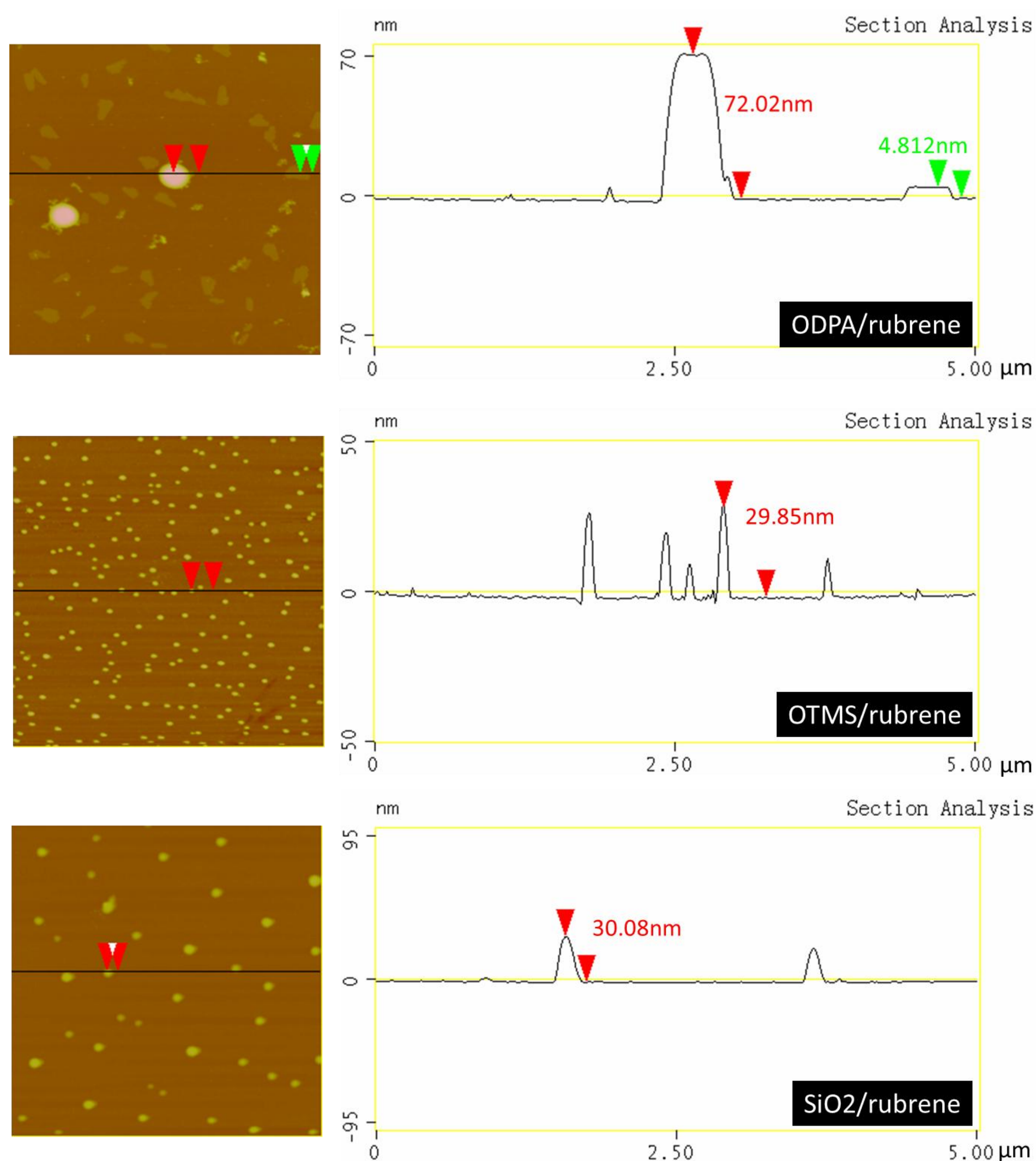

Figure S-10 AFM section analysis for films of rubrene with the norminal thickness of 3 nm deposited on the surfaces of (a) ODPA-modified SiO_2, (b) OTMS-modified SiO_2, (c) bare SiO_2.