Electronic Supplementary Information

Poly(3-hexylthiophene) Monolayer Nanowhiskers

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Experimental Section

Materials. Regioregular P3HT was purchased from Rieke Metals Inc. and used as received. Molecular weight (Mn = 16000 g/mol, PDI = 1.9) values were determined by gel permeation chromatography against polystyrene standards. H-T regioregularity was measured by comparing the ratio of signals at 2.8 and 2.6 ppm in nuclear magnetic resonance[1] to be 98%. Chloroform was purchased from Beijing Chemical Reagents Company and used as received. Water was purified with a PGeneral GWA-UN4 unit (18.2 MΩ.cm).

Substrate. Silicon wafers and quartz slides were cleaned in boiling piranha solution (H_2SO_4/H_2O_2 = 30:70 v/v), rinsed with adequate ultrapure water and dried with a stream of nitrogen.

Sample preparation. P3HT was dissolved in refluxing chloroform (0.1 $mg.mL^{-1}$) with stirring, and and the solution was stored in a sealed vessel in darkness at 20 ± 2 °C for 1 week. Si or quartz substrates were dipped into P3HT solutions for 1 min. Then some of these substrates were immersed in chloroform immediately for 1 min rinse and then dried, and others were dried directly without this rinsing in chloroform. Normal nanowhiskers were prepared following a literature procedure[2] by addition of 12 mL of n-hexane dropwise into 3 mL of P3HT chloroform solution (0.5 $mg.mL^{-1}$).

Characterization. AFM images were obtained using an Agilent 5500 Scanning Probe Microscope in tapping mode with Si tips with radius less than 10 nm and resonance frequency of 250-300 KHz. A droplet of solution was dried on copper grids coated with carbon film for TEM tests, which were performed on a JEOL JEM-1011 microscope (100 kV); the camera length was calibrated with Au. UV-vis spectra were acquired using a Hitachi U-3900 spectrophotometer. GIXRD was performed on a Bruker D8 Discover diffractometer equipped with a copper target (λ_{ka} = 0.154 nm) at 2θ of 3~25° at a speed of 1°/min.

FETs. Si wafers with a 500 nm insulating layer (SiO_2) were successively cleaned with water, acetone, piranha solution, water, and isopropanol, and dried with nitrogen. The substrates were dipped into P3HT solution for 10 min (in order to collect more monolayer nanowhiskers to cover the substrate) and then into chloroform for 1 min. Then top-contact devices were fabricated on the substrates, with Au electrodes used as source and drain, and the channel length and width of device 26 and 203 μm, respectively. The morphology of the device was characterized by AFM (Veeco Nanscopy IIID, USA). Electrical characteristics of the devices were recorded with a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station in a clean and shielded box in ambient. According to the transfer characteristics, the mobility was calculated from following formula,

$$I_{SD} = \frac{W}{L} \mu C (V_G - V_T) V_{SD}$$

where μ is the field-effect mobility, W is the channel width, L is the channel length, and C is the capacitance of gate insulator per unit area, respectively.

REFERENCES

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(2) L. G. Li, G. H. Lu and X. N. Yang, *J. Mater. Chem.,* 2008, **18**, 1984.

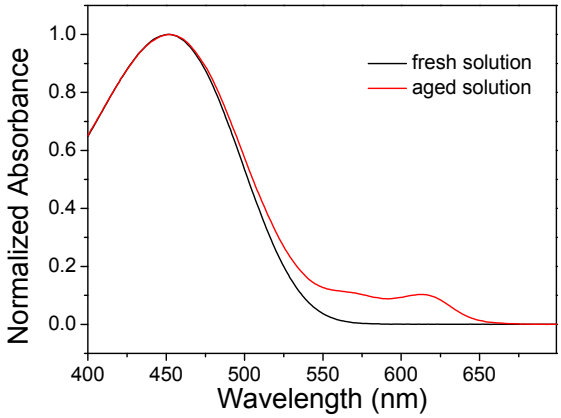

Figure S1. UV-vis spectra of fresh and aged P3HT/chloroform solution.

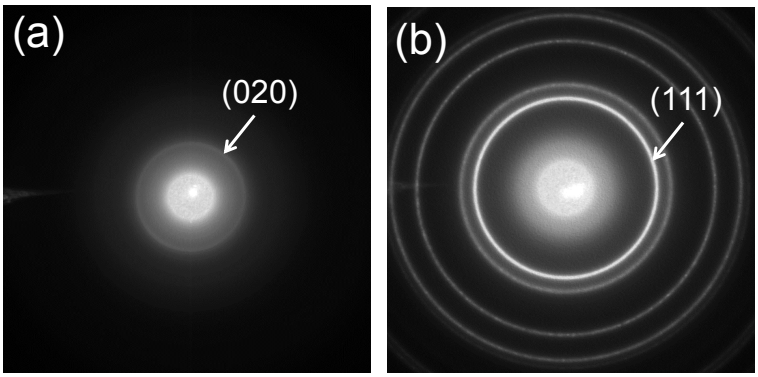

Figure S2. SAED patterns of (a) P3HT monolayer nanowhiksers and (b) thin gold film obtained under the same condition and shown in the same scale. The crystal plane distance $d_{P3HT(020)}$ can be obtained by $d_{P3HT}.R_{P3HT} = d_{Au}.R_{Au}$, where R is the distance between the diffraction ring and central spot, and $d_{Au(111)}$ = 0.2355 nm.

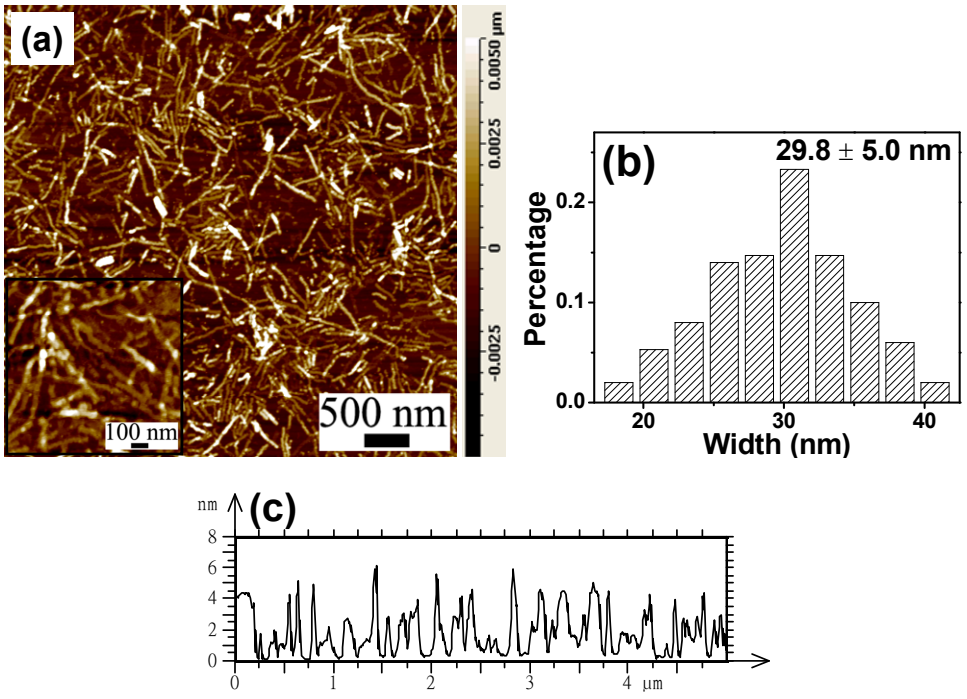

Figure S3. (a) AFM topography image of normal nanowhiskers prepared by the "whisker methods" from the same P3HT sample (inset is an enlarged view), and (b) width distribution and (c) typical cross section profile of (a).

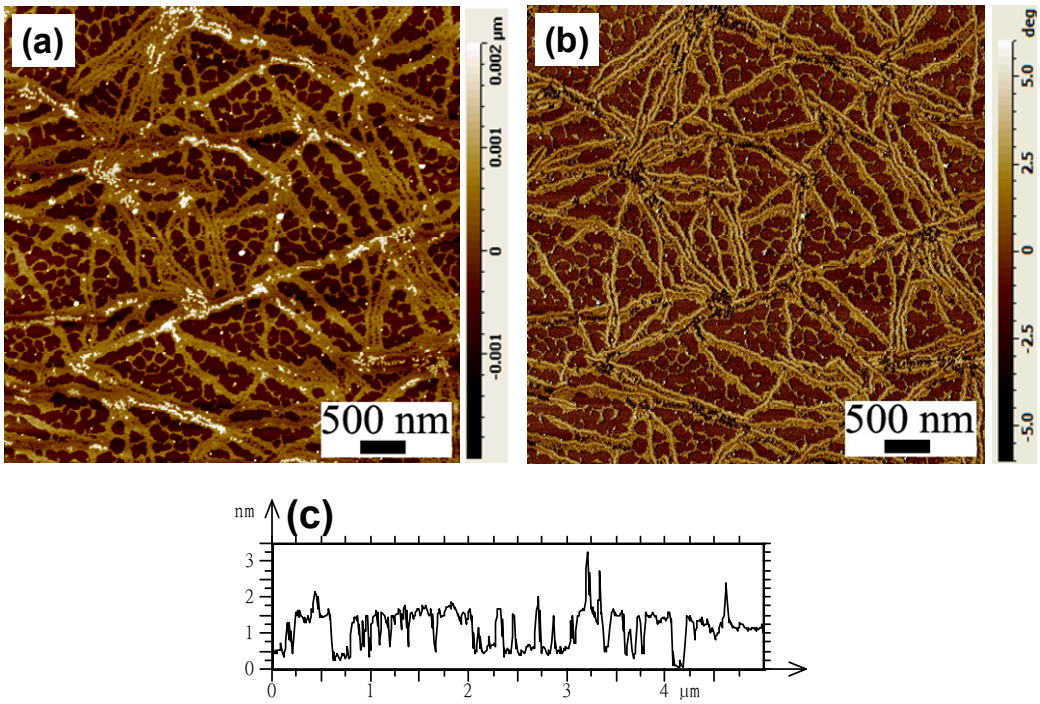

Figure S4. AFM topography (a) and phase (b) images of the P3HT monolayer nanowhiskers collected on Si wafer and dried without rinsing with chloroform. Nanocrystals can be distinguished from disordered P3HT molecules due to their different viscoelastic responses in the phase image. (c) Typical

cross section profile of (a), where height values of 2-3 nm are observed at some spots, obviously due to monolayer nanowhiskers overlaid by other crystalline or amorphous material.

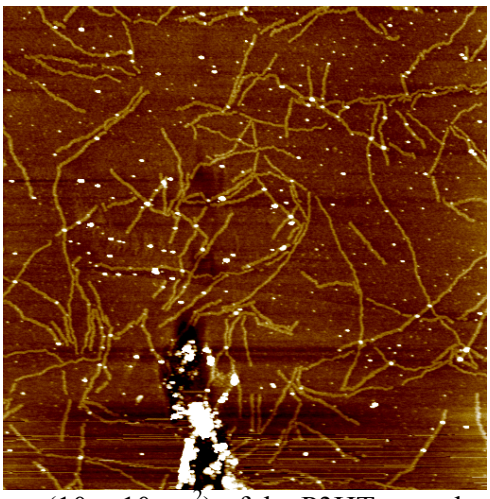

Figure S5. AFM topography image ($10 \times 10\mu m^2$) of the P3HT monolayer nanowhiskers collected on Si wafer from solution aged for 1 day.

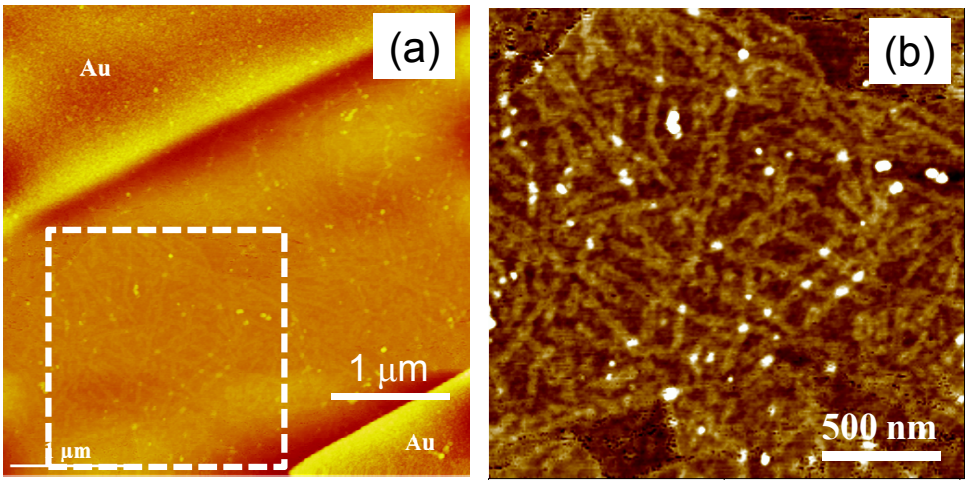

Figure S6. (a) AFM topography image of the P3HT monolayer nanowhiskers collected on a Si wafer used for FET measurements with Au electrodes. (b) An enlarged view of the area in the square marked by the dashed lines in (a).