

## Supporting Information Available

### Single Crystals of Polythiophene with Different Molecular Conformations Obtained by Tetrahydrofuran-Vapor Annealing and Controlling Solvent Evaporation

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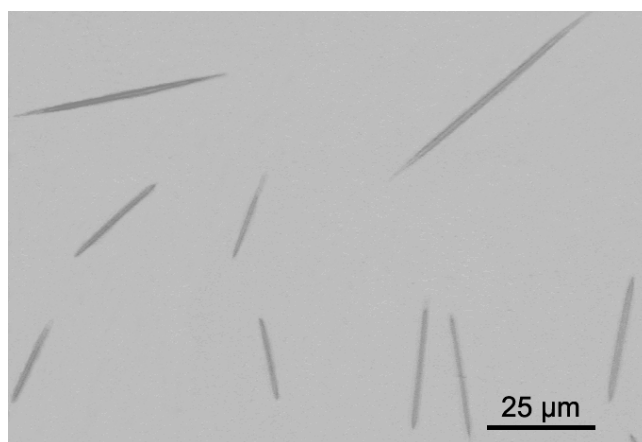
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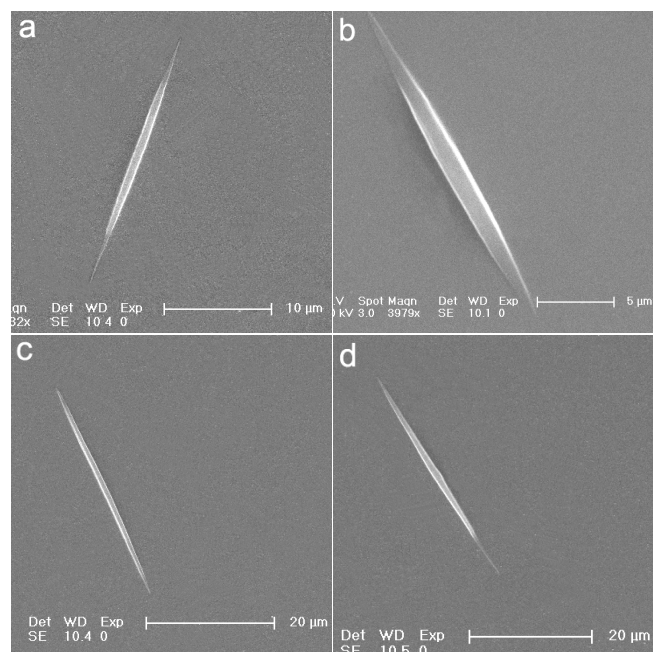
Needle-like single crystals of poly(3-hexylthiophene) (P3HT) can be obtained from the initial solution-cast polycrystalline film by tetrahydrofuran vapor annealing. When the film has been annealed at 35°C for 42 h, the obtained crystals possess the length of 20-60  $\mu\text{m}$  and the diameter of 1-2.2  $\mu\text{m}$ . The optical and SEM images of the crystals are shown in Figure S1 and Figure S2, respectively. The detailed AFM height image of a fully-grown P3HT single crystal is shown in Figure S3, and the AFM height image of a P3HT crystal with the length of about 10  $\mu\text{m}$  is shown in Figure S4.

The schematic illustration for the configuration of field effect transistor (FET) base on the single crystals is manifested in Figure S5a. SEM image of the P3HT single crystal measured is shown in Figure S5b. For this FET,  $W$  is 1.3  $\mu\text{m}$ ,  $L$  is 20  $\mu\text{m}$ , and  $C_i$  is 22 nF/cm<sup>2</sup>. The on/off current ratio is 40 and the threshold voltage is 8.1 V. SEM image of the P3OT single crystal measured is shown in Figure S5c. For this FET,  $W$  is 500 nm,  $L$  is 32  $\mu\text{m}$ ,  $C_i$  is 22 nF/cm<sup>2</sup>. The on/off current ratio is 360 and the threshold voltage is 5.2 V.

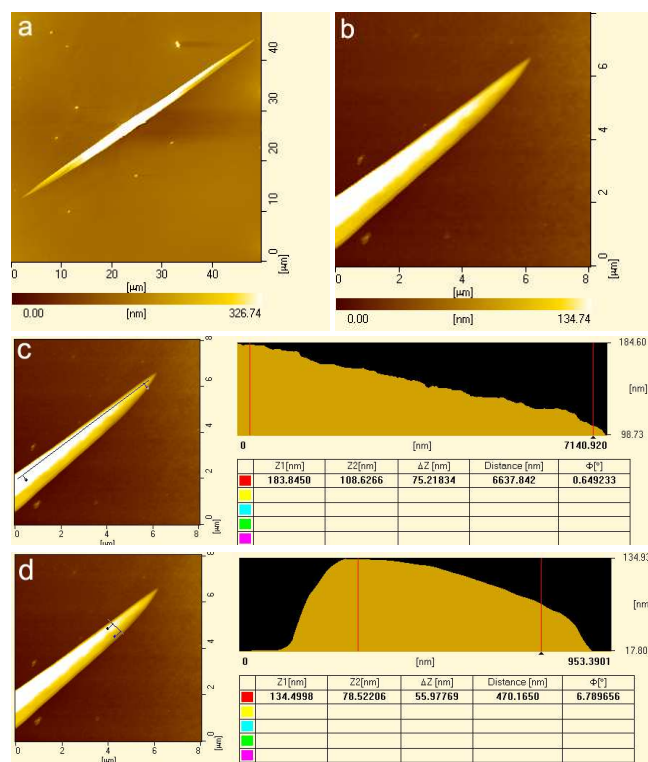
Rod-like single crystals of poly(3-octylthiophene) (P3OT) can be obtained by controlling solvent evaporating speed, and the crystals are of the length of 3-50  $\mu\text{m}$ , the width of 150-800 nm, and the height of several hundred nanometers. The optical and SEM images of the P3OT single crystals are shown in Figure S6 and Figure S7, respectively. The detailed AFM height image of a P3OT single crystal is shown in Figure S8.



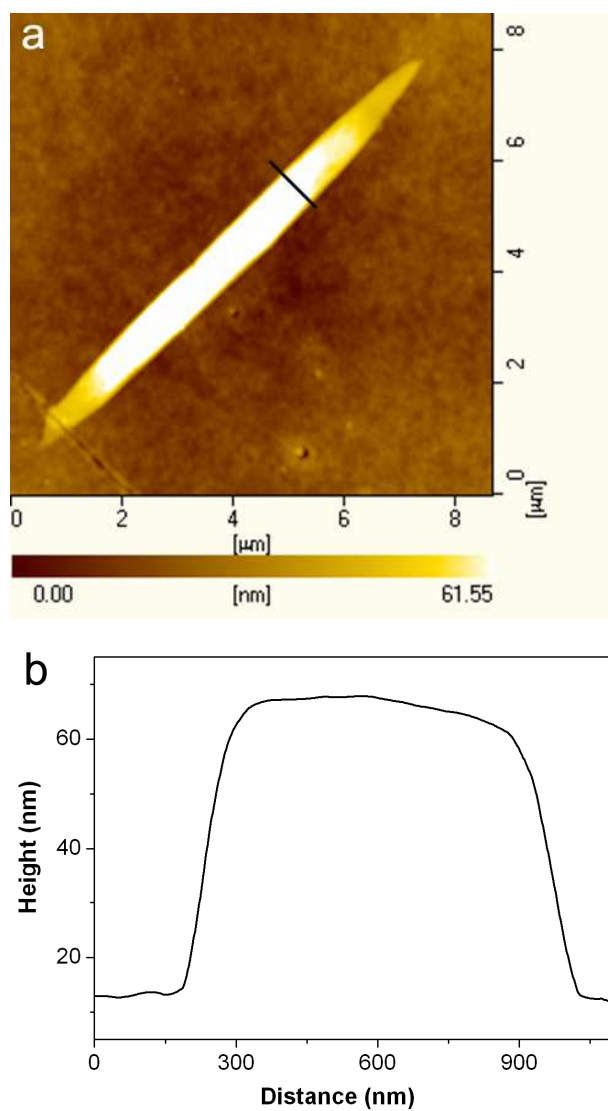
**Figure S1.** Optical images of the P3HT single crystals obtained by THF vapor annealing.



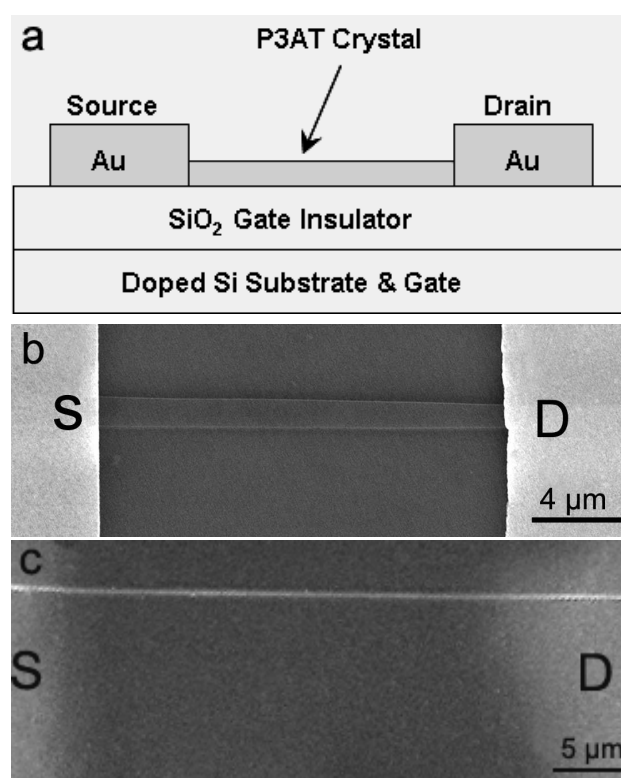
**Figure S2.** SEM images of the P3HT single crystals with different sizes.



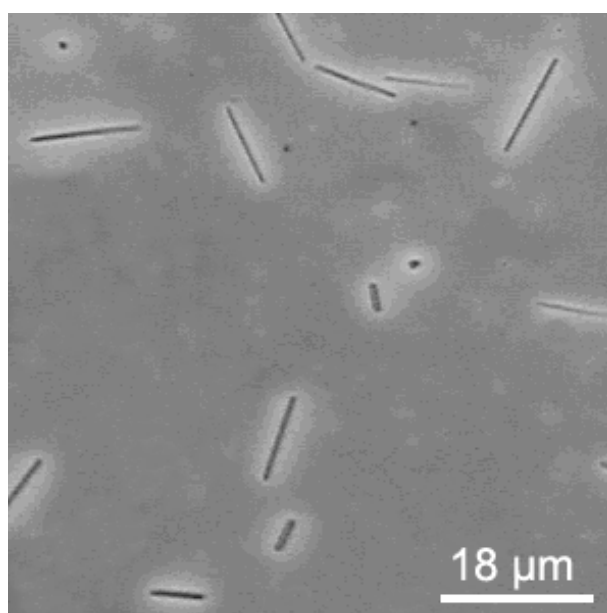
**Figure S3.** AFM height image of a P3HT single crystal (a) and the detailed image of its part (b). The corresponding thickness along the length axis (c) and cross section (d) of the crystal.



**Figure S4.** (a)AFM height image of a P3HT crystal with the length of about 10  $\mu\text{m}$ . (b) The height profile of the solid line in (a).

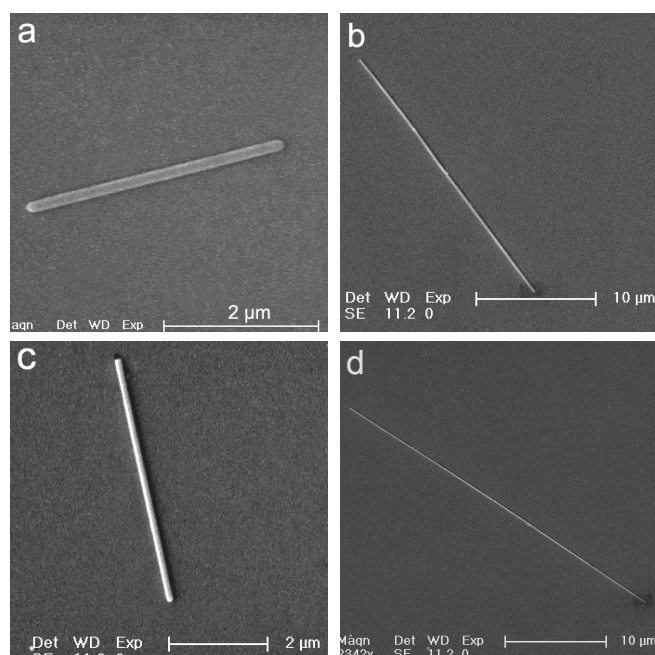


**Figure S5.** (a) Illustration for the configuration of the FET base on the P3AT single crystals. (b) SEM image of the P3HT single crystal measured. (c) SEM image of the P3OT single crystal measured.

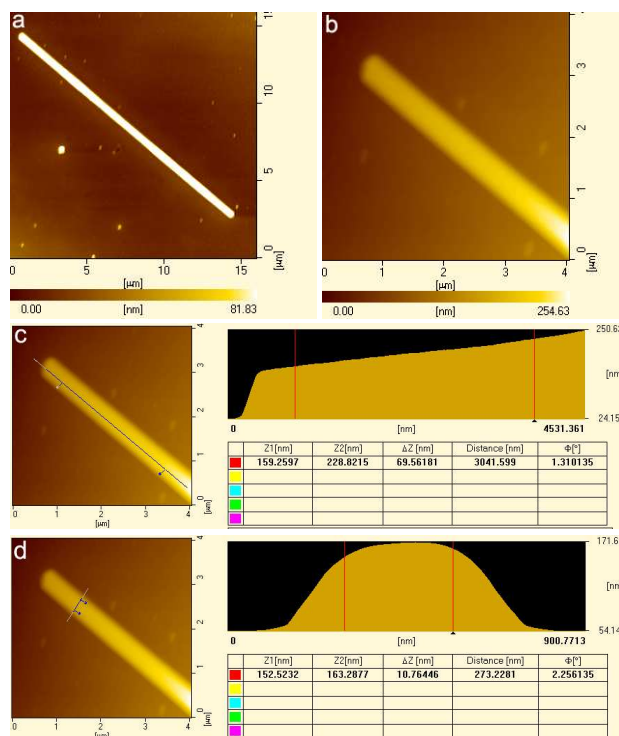


**Figure S6.** Optical images of the P3OT single crystals obtained by controlling solvent evaporation.





**Figure S7.** SEM images of the P3OT single crystals with different sizes.



**Figure S8.** AFM height image of a P3OT single crystal (a) and the detailed image of its part (b). The corresponding thickness along the length axis (c) and cross section (d) of the crystal.