*Electronic Supplementary Information*

# Conformation Modification of Terthiophene During On-Surface Synthesis of Pure Polythiophene

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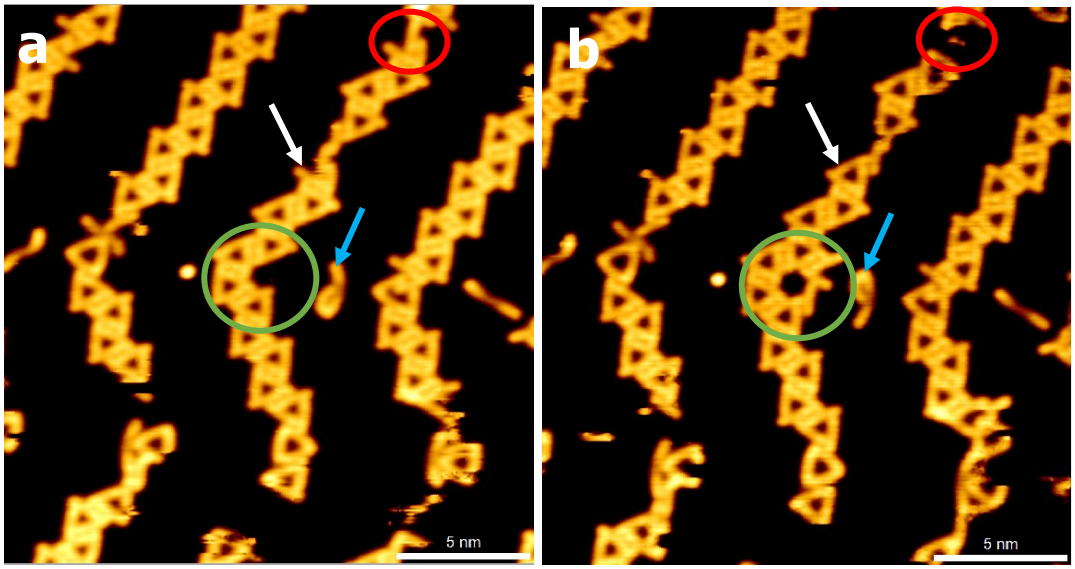
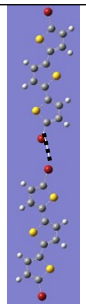
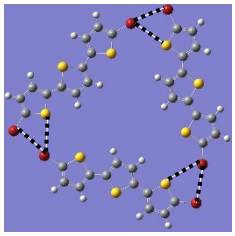



**Figure S1**. Two sequences of images for the triangle self-assembled pattern of DBTT showing the tip disturbance could move the triangles easily. (Scan area: 100×100 nm$^2$; $V_s$ = –1000 mV, $I$ = 100 pA).

**Table S1.** Calculated building blocks, structural parameters, interaction energies and topological properties of the electron density at the critical points to bromine atoms in different aggregations for DBTT.

| Molecular block |  |  | |
|---|---|---|---|
| Bond | C–Br···Br | C–Br···Br | C–Br···S |
| Distance (Å) | 3.41 | 3.43 | 3.63 |
| Angle (°) | 150 | 172 | 120 |
| $\Delta E$ (kcal mol$^{-1}$) | –0.26 | –2.58 | |
| $\rho_{BCP}$ (e Å$^{-3}$) | 0.062 | 0.069 | 0.046 |
| $\nabla^2\rho_{BCP}$ (e Å$^{-5}$) | 0.794 | 0.83 | 0.51 |
| $G_{BCP}$ (kJ mol$^{-1}$ bohr$^{-3}$) | 16.78 | 18.00 | 11.10 |
| $V_{BCP}$ (kJ mol$^{-1}$ bohr$^{-3}$) | –11.91 | –13.34 | –8.26 |
| $H_{BCP}$ (kJ mol$^{-1}$ bohr$^{-3}$) | 4.87 | 4.64 | 2.86 |
| $\mid V_{BCP} \mid /G_{BCP}$ | 0.71 | 0.74 | 0.74 |

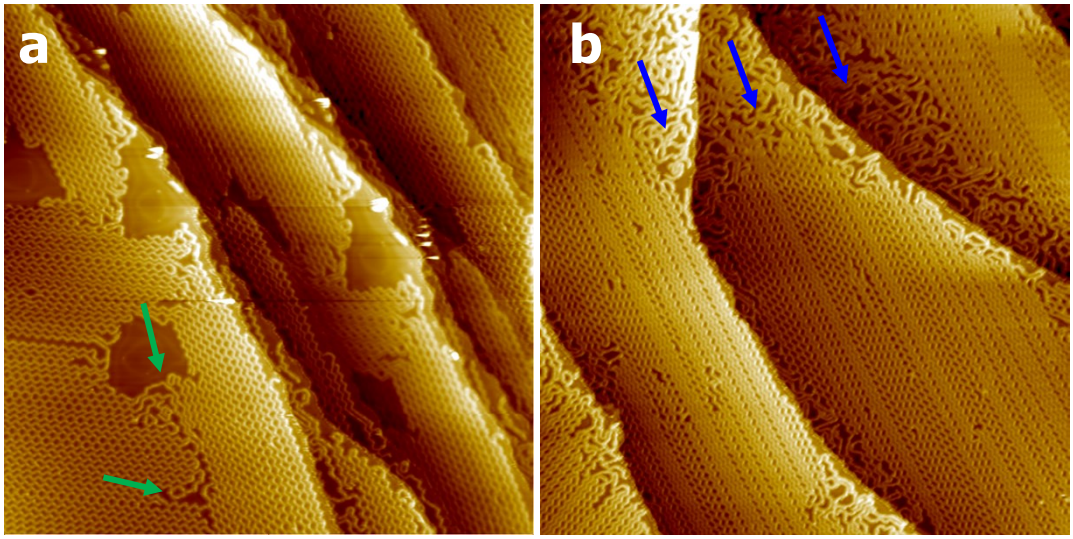



**Figure S2**. Large-scale STM images showing the initial formation of the polythiophene at the boundary of the domains as the red arrows indicated in Figure a and the step edge of the Au(111) as the blue arrows indicated in Figure b. (a) Heating the sample for 30 min from the room temperature to 150℃. (Scan area: 100×100 $nm^2$, $V_s$ = 600 mV, $I$ = 100 pA) (b) Heating the sample for 30 min from the room temperature to 120℃, then annealing the sample at 170℃ for 10 min. (Scan area: 100×100 $nm^2$, $V_s$ = 800 mV, $I$ = 50 pA).

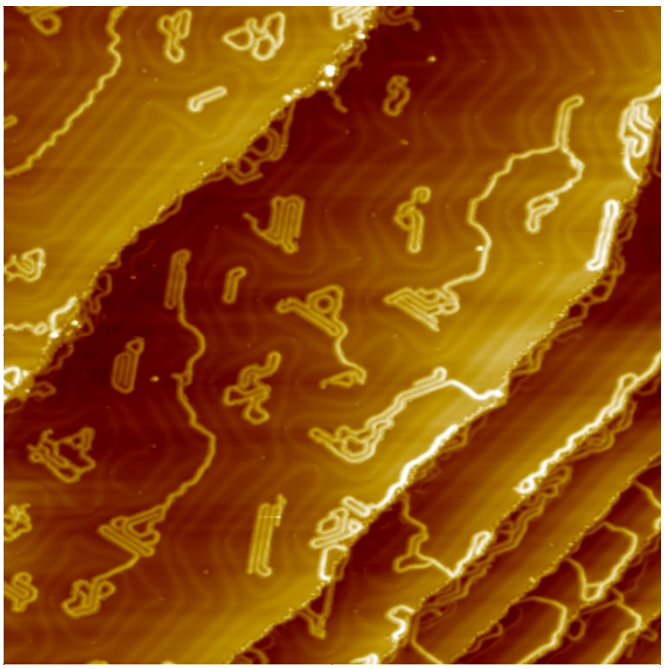


**Figure S3**. Large-scale STM image showing the formation of polythiophene. Almost no Br atoms adsorb on the Au(111) surface. The herringbone reconstruction of Au(111) is distorted at the place where the polythiophene coils are formed. Heating the sample for 40 min from the room temperature to 190℃. (Scan area: 66×66 $nm^2$, $V_s$ = –800 mV, $I$ = 80 pA)

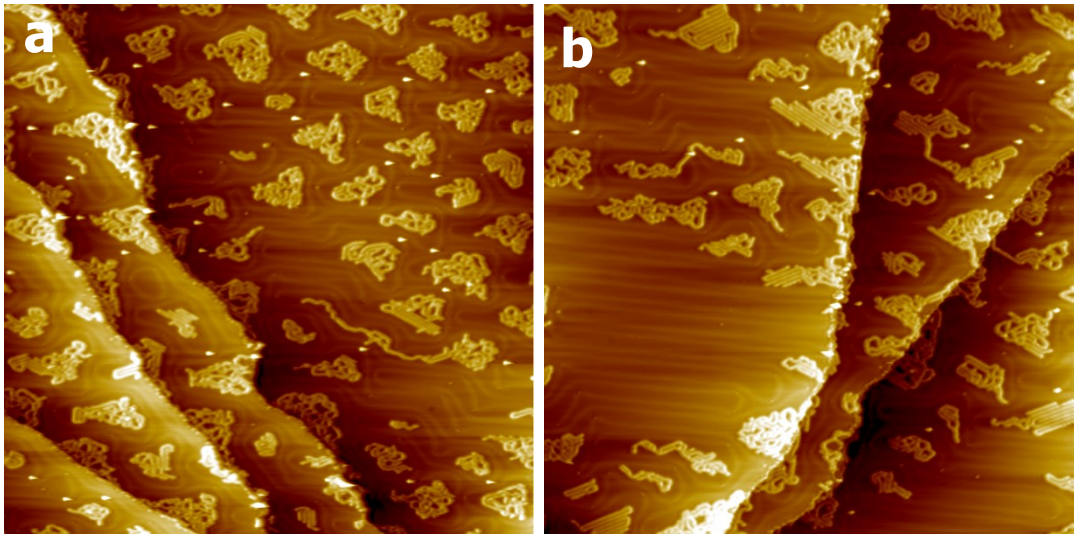



**Figure S4**. Large-scale STM images showing the morphology change of polythiophene coils from relative disordered (a) to less ordered coils (b) after annealing at 295℃ for 5 min. (a) Scan area: 100×100 nm$^2$; $V_s$ = 600 mV, $I$ = 200 pA. (b) Scan area: 95×95 nm$^2$; $V_s$ = 700 mV, $I$ = 50 pA.

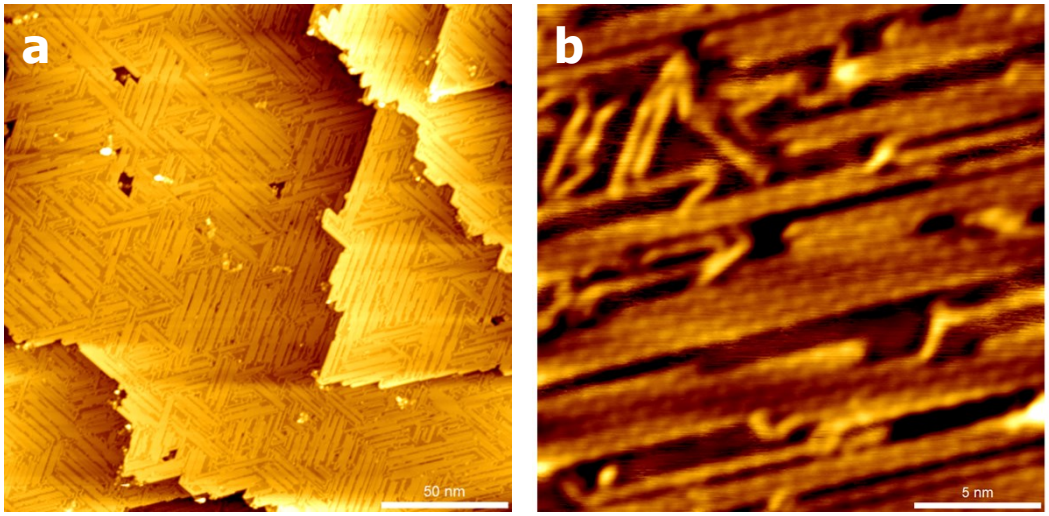



**Figure S5.** Large-scale (a) and high-resolution (b) STM images taken after deposition of 0.8 monolayer DBTT onto Cu(111) held at room temperature, showing the formation the organometallic coordination. ($V_s$ = – 400 mV, $I$ = 300 pA).

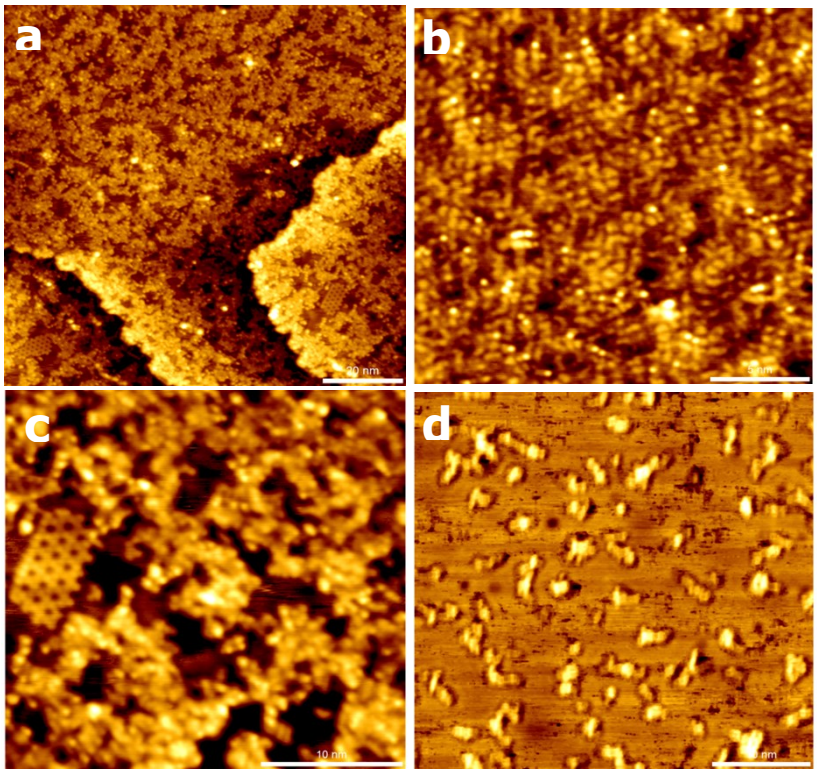



**Figure S6.** (a-c) STM images taken after annealing the coordinated intermediate of DBTT with 0.8 monolayer at 200 ℃. ($V_s$ = 600 mV, $I$ = 200 pA). (d) STM image taken after annealing the coordinated intermediate of DBTT with 0.2 monolayer at 200 ℃. ($V_s$ = –500 mV, $I$ = 200 pA).

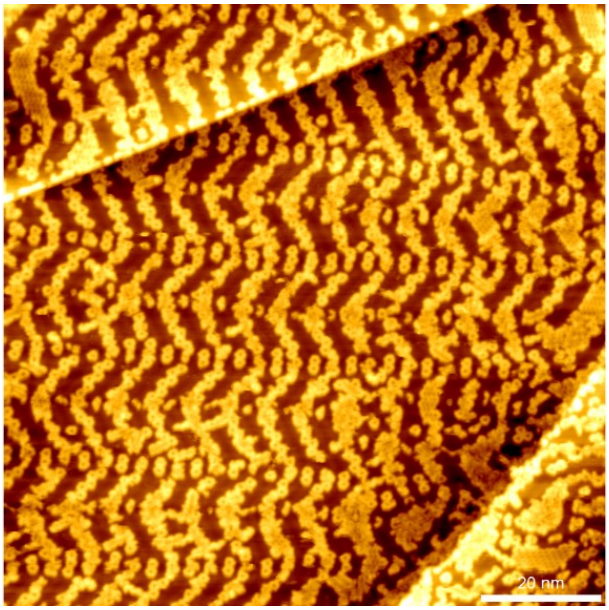



**Figure S7.** Large-scale STM image showing the molecular self-assembly after deposition of DBTT-$CH_3$ on the Au(111) surface at room temperature with ~0.6 monolayer. ($V_s$ = 1000 mV, $I$ = 70 pA).

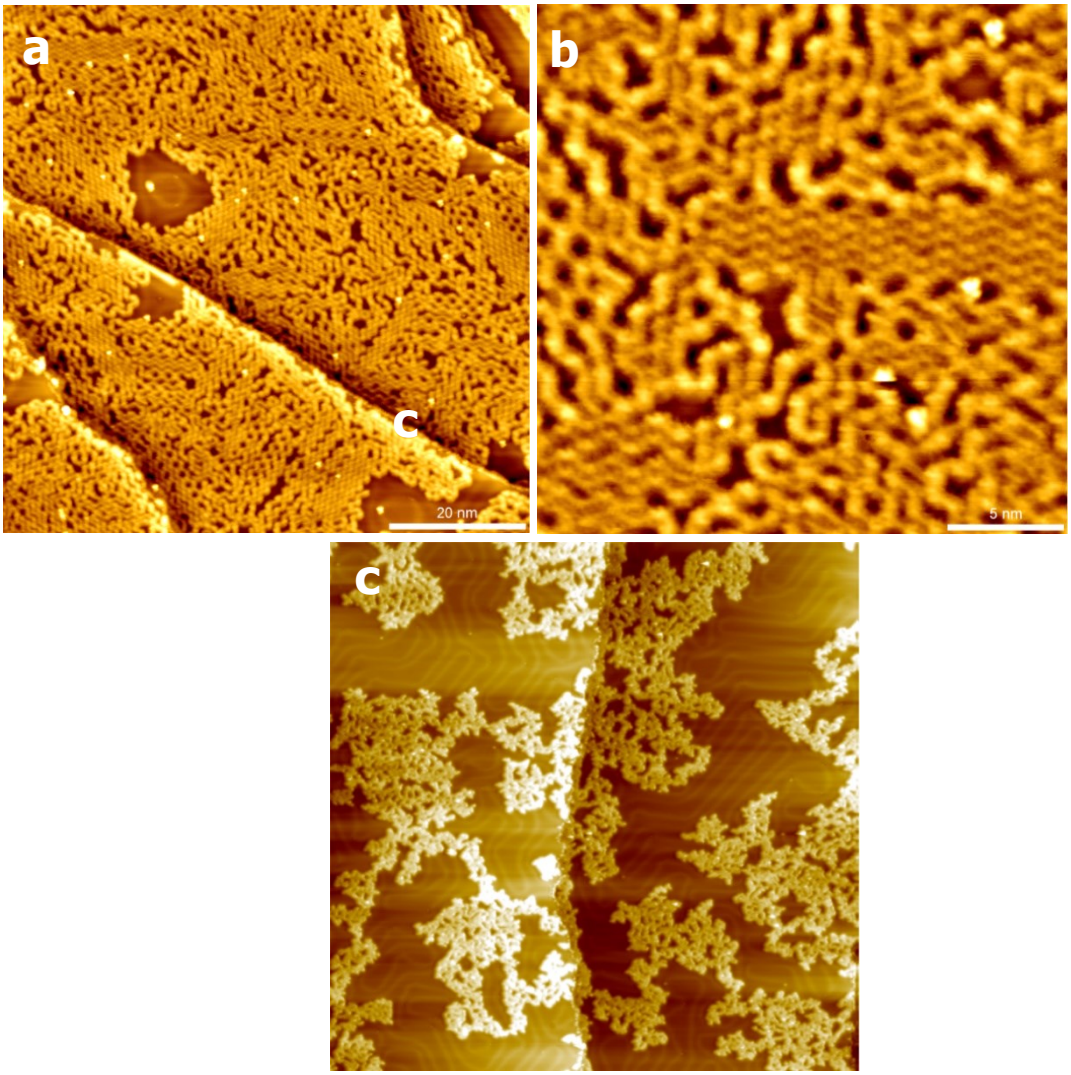



**Figure S8**. (a) Large-scale STM image showing the organometallic intermediate of DBTT-$CH_3$ deposited on the Au(111) surface at 150 ℃ with 0.5 monolayer with the zigzag chains. ($V_s$ = –800 mV, $I$ = 100 pA). (b) STM image showing the close-packed chains with adsorbed bromine atoms and the cavity formed resulting from the absence of some bromine atoms. ($V_s$ = –800 mV, $I$ = 100 pA). (c) STM image of the completely polythiophene from DBTT-$CH_3$ at a coverage of 0.6 monolayer on the Au(111) surface annealing at 200 $^0$C. (Scan area: 50 × 50 nm$^2$; $V_s$ = 600 mV, $I$ = 70 pA).

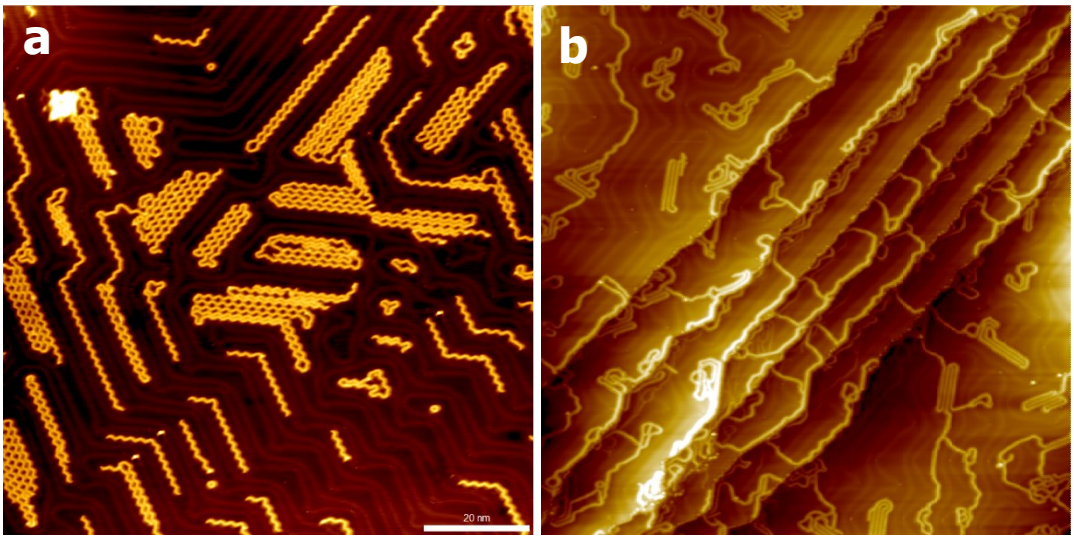



**Figure S9.** (a) Large-scale STM image of the organometallic intermediate of DBTT showing the single lines located on the Au(111) surface. ($V_s$ = –600 mV, $I$ = 60 pA). (b) Large-scale STM image of the complete polymer of DBTT showing the ordered and disorder polymer chains on the Au(111) surface. Scan area: 100 × 100 nm$^2$; $V_s$ = 500 mV, $I$ = 200 pA.

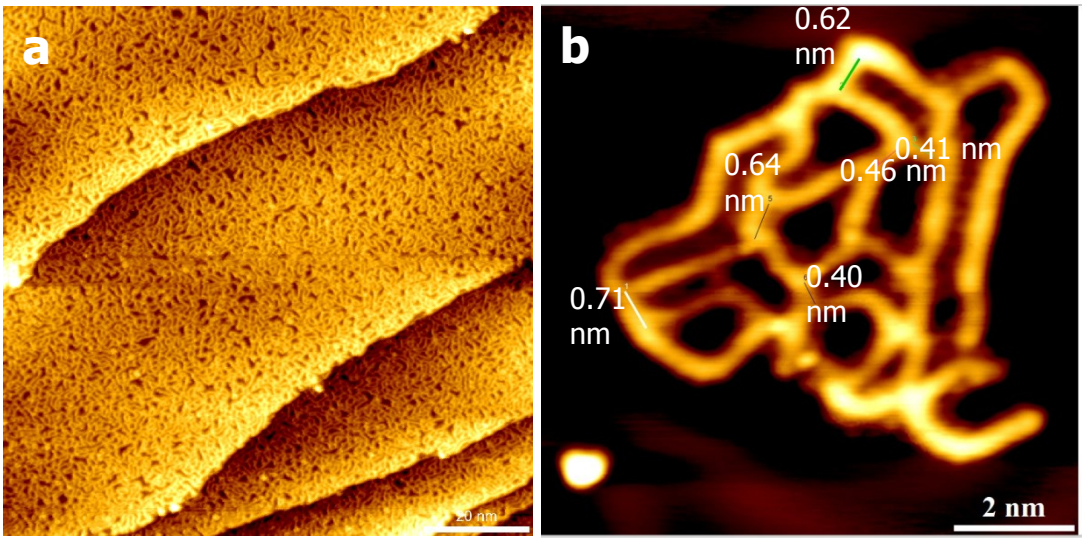



**Figure S10.** (a) Large-scale STM image of the complete polymer of DBTT showing the network flexible polymer. $V_s$ = 550 mV, $I$ = 90 pA. (b) High-resolution STM image for one cluster of polythiophene network showing the distance between some adjacent junction points.