

Supporting Information

Side-Functionalized Two-Dimensional Polymers Synthesized via On-Surface Schiff-Base Coupling

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1. Experimental details

BTA, DHI, DMA, dimethylsulfoxide (DMSO) were purchased from J&K and used without further purification. For sample preparation of 2D polymers on HOPG surface, the monomers were first dissolved in DMSO with a mass concentration of 1 mg/g respectively. Then the aromatic amine and aldehyde were mixed with mole ratio of about 3:1. Then the solutions were diluted 100 times. An amount of ~5 μ L of the solution was drop-cast on the freshly cleaved surface of HOPG. The drop-cast samples were positioned in a preheated vacuum oven and subject to the designated temperature. The optimal conditions for -OH functionalized 2DP_{BTA-DHI} are 75 °C for 4 hours. The conditions for 2DP_{BTA-DMA} are 140 °C for 30 min. The sample was characterized with STM at the solid/air interface at room temperature. STM measurements were performed on an Agilent 5100 scanning probe microscopy with mechanically formed Pt/Ir (80/20) tips under ambient conditions. All images were taken with the constant current mode. The calibration of STM images were carried out by using HOPG lattice with atomic resolution. The chemical structure models were built by the HyperChem software.

2. Extra STM images

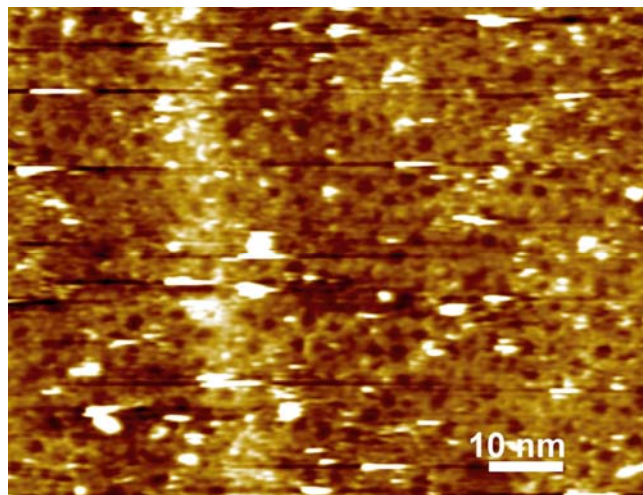


Figure S1. Large-scale STM image of 2DP_{BTA-DHI} obtained at 75°C for 30 mins. The tunneling conditions were $I_{\text{set}} = 0.015$ nA, $V_{\text{bias}} = 0.5$ V.

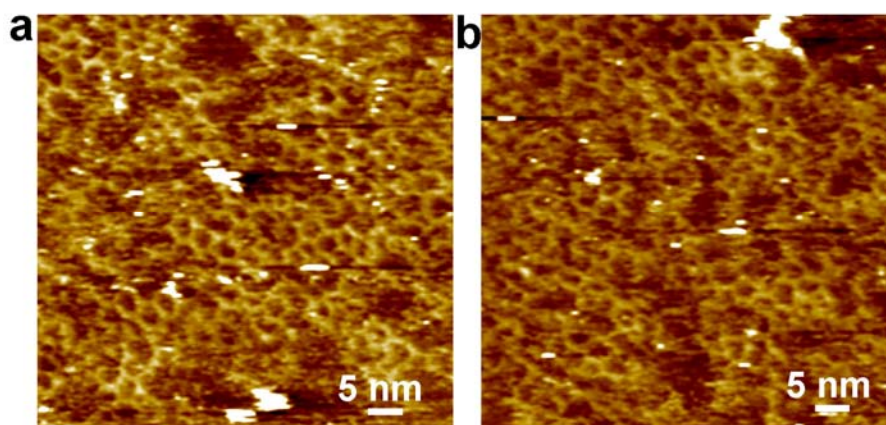


Figure S2. STM images of 2DP_{BTA-DHI} obtained at 140°C for 30 mins. The tunneling conditions were $I_{\text{set}} = 0.3$ nA, $V_{\text{bias}} = 0.5$ V.

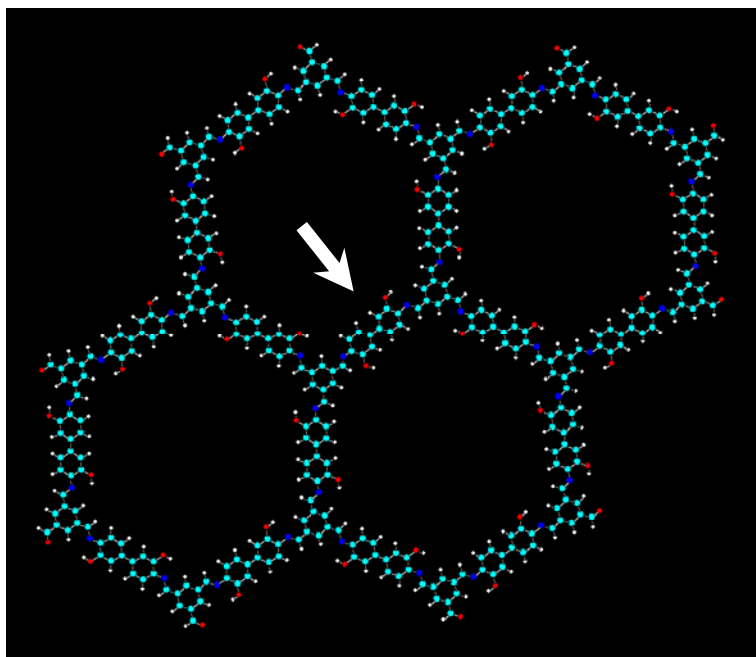


Figure S3. An optimized lattice of 2DP_{BTA-DHI} with most of the imine groups adapting *trans*-conformation, while only one edge of the hexagon adapting *cis*-conformation (highlighted with the white arrow). No observable distortion of the lattice can be observed.

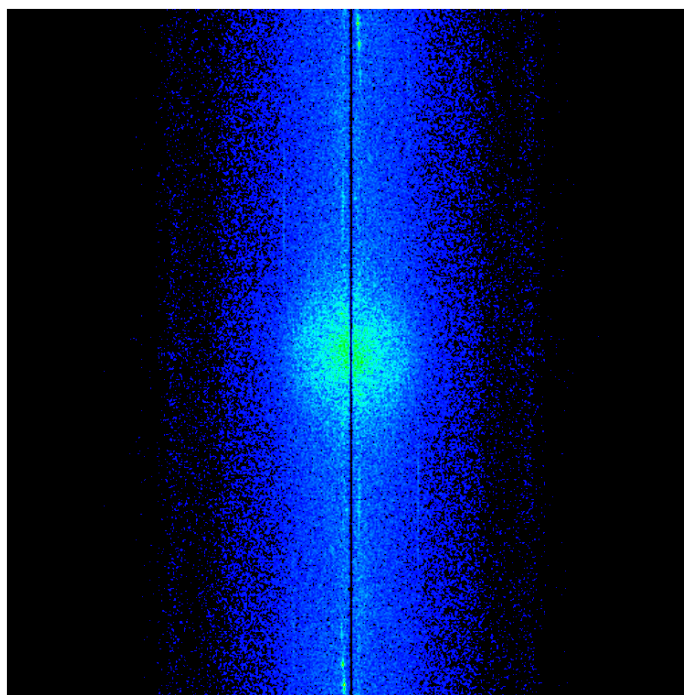


Figure S4. Corresponding FFT of STM image shown in Figure 3d in the main text.

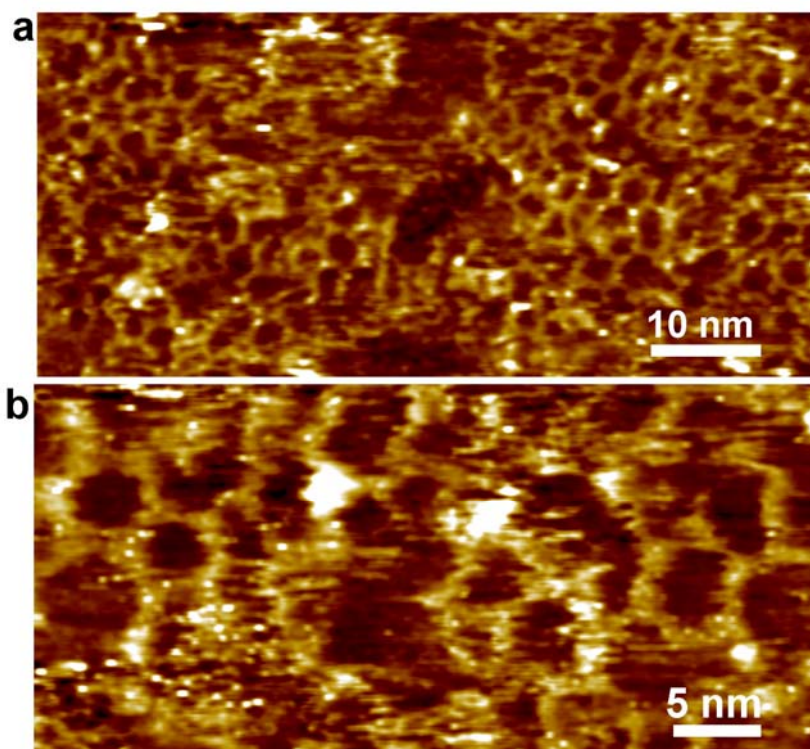


Figure S5. (a) Large-scale STM image of 2DP_{BTA-DHI} obtained at 205°C for 11 hours. (b) High resolution STM image of 2DP_{BTA-DHI} obtained at 205°C for 11 hours. The tunneling conditions were $I_{\text{set}} = 0.1 \text{ nA}$, $V_{\text{bias}} = 0.5 \text{ V}$.

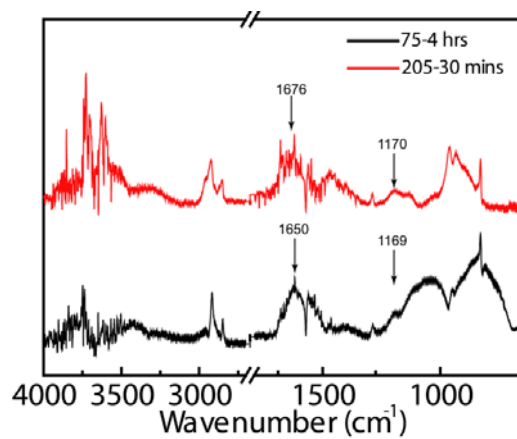


Figure S6. ATR-FT IR of 2D polymers obtained after annealing at 75 °C for 4 hours and 205 °C for 30 mins, respectively.

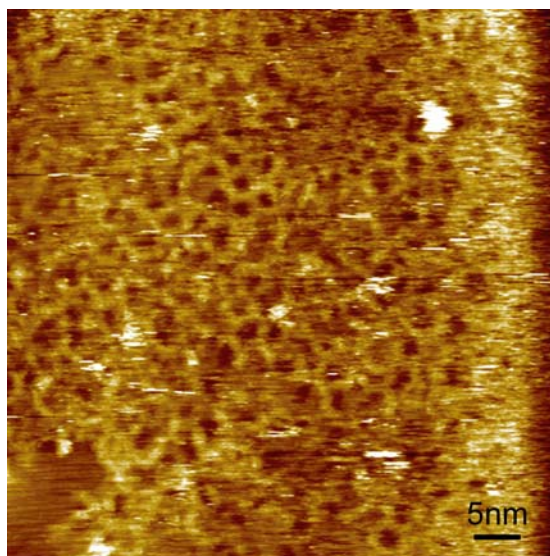


Figure S7. STM image of the 2DP_{BTA-DHI} prepared in a tube furnace with argon protection at 75°C for 4 hours. The network still appears defective. This is probably because the cyclization of imine with the *o*-OH group to form oxazolidine do not need the presence of oxidant, thus argon protection can not prevent the cyclization. The tunneling conditions were $I_{\text{set}} = 0.1 \text{ nA}$, $V_{\text{bias}} = 0.5 \text{ V}$.