Supplementary Information for

Self-Organized and Cu-Coordinated Surface Linear Polymerization

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1. Bias dependent STM images of the polymerized structures

We carried out bias dependent STM images at various bias voltages. Imaging at relative high bias (Fig. S1a and S1b) integrates many molecular orbitals, which blurs the detail molecular structures. The detailed structure becomes clearer at lower bias (Fig. S1c), in which we can see that the linear structure shows as a wavy line, decorated with bright dots at both sides.
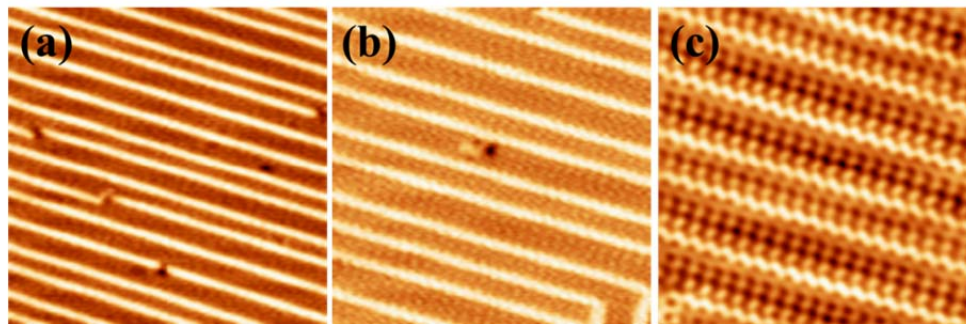

Figure S1 Bias dependent STM images of the polymerized structure. Bias voltage is 1 V for (a), 100 mV for (b) and 16 mV for (c). Tunneling current is 100 pA.

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2.Evolution of the "circuit-board" pattern

Although the depolymerized phase is stable at 28 K, the phenylvinylidene derivatives polymerizes again at elevated temperature. At 85 K, we continuously scanning a target region using positive bias (+1 V) and mark the linear structure along [001] and [010] with different colors. One can see that the "circuit-board" pattern moves upon the continuous scanning, indicating the depolymerization under positive voltage scanning and the subsequence polymerization due to the thermal fluctuations.
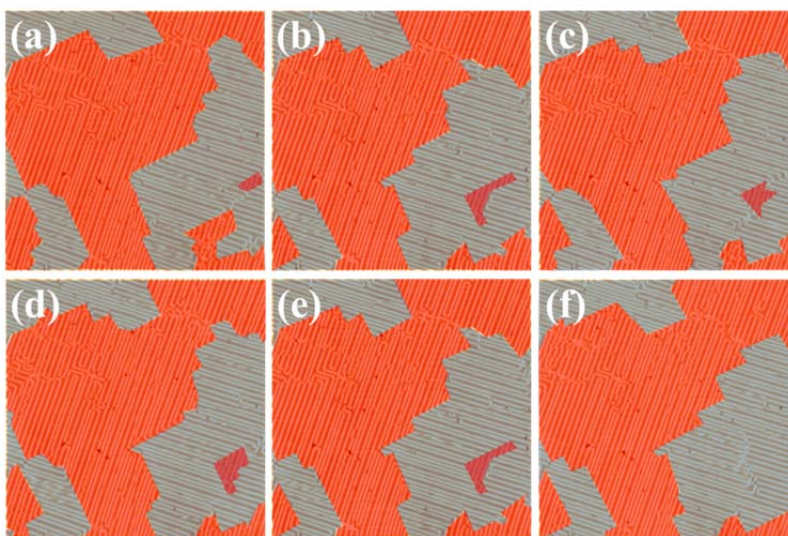

Figure S2 Continuously scanned STM images. Bias voltage is 1V. Tunneling current is 100 pA. Image size is 60 nm×60 nm.

3. Relaxed structural model and the simulated STM image of the depolymerized phase

Following the earlier calculations by Ford *et al.*[1], there exist three derivatives of the ethynyl group that will produce an upright orientation: (1) surface-bonded Ph-C≡C● species, which involves the dissociation of the proton; (2) styrene-derivative, involves partial dissociation of the triple bond; and (3) vinylidene structure, involves tautomerization of the ethyne group, with the proton moving to the C2 position to form a bonded phenylvinylidene. Among these configurations, Ph-C≡C● species and phenylvinylidene are perpendicularly bonded to surface, while styrene-derivative is bonding with the C-C ethylene axis approximately parallel to the surface and the phenyl ring tilting upright. The flat-lying and styrene derivative can be immediately ruled out

because of their large lateral size for which the molecules[2, 3] cannot form such a compact structure (Fig. S3a). The phenylvinylidene derivative, however, cannot form a linear polymer. Therefore, the compact ordering of molecules can only attribute to the Ph-C≡C• species configuration, in which phenylacetylene have one hydrogen atom desorbs and bonds perpendicular with the metal surface. A relaxed structural model and the simulated STM image for this four-fold Ph-C≡C• species assembly are shown in Fig. S3b and S3c, respectively. The simulated image exhibits good agreement with the experimental ones (Fig. S3a). The tip induced depolymerization experiments strongly supported our argument that the "circuit board" pattern is composed of polymerized molecules and the observed polymer bonds with the Cu substrate covalently via the hydrogen desorption.
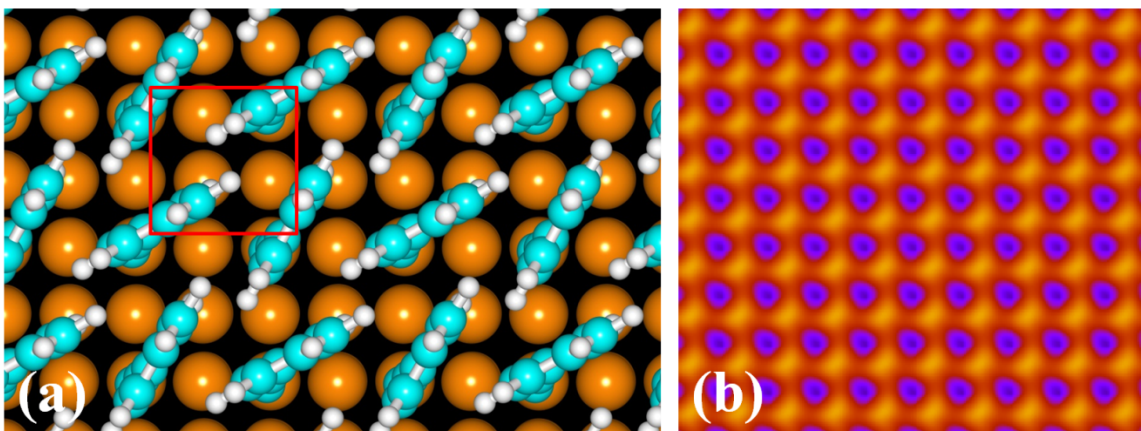

Figure S3 Relaxed structural model and the simulated STM image of the depolymerized phase. (a) Relaxed structural model of the depolymerized condensed phase. (b) Simulated STM image of the depolymerized condensed phase.

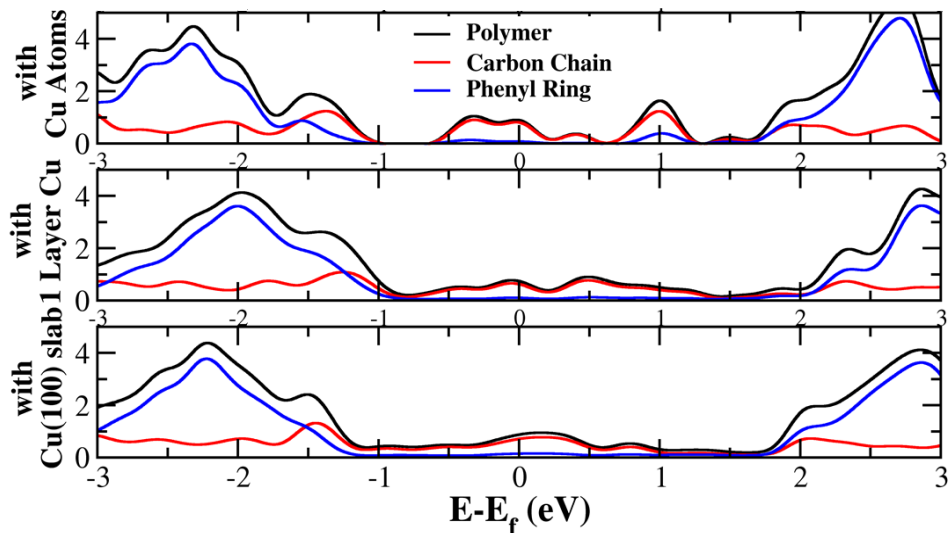**4. Calculated PDOS for chemisorbed polymer on Cu(100)**

Fig. S4. Calculated PDOSs for poly(phenylacetylenyl)s bonding with Cu atoms, poly(phenylacetylenyl)s placed on one layer copper and on four layers of copper (aligned with Fermi level).

5. Deprotonation Energy

The energy for deprotonation was calculated as follows. We considered two systems: system 1 is composed of one PA molecule in gas-phase and a bare Cu(100) surface; system 2 is composed of one deprotonated PA molecule deposited on Cu(100), with the corresponding H atom placed nearby the deprotonated PA molecule and deposited on Cu(100) as well. By comparing the energetics of system 1 and system 2, we find that the energy gained in going from system 1 to system 2 is 0.79 eV. Thus, the deprotonation by deposition of PA molecules on Cu(100) is energetically favored.

The energetics related above are:

System 1

PA in gas-phase = -.91987408E+02

Bare Cu substrate = -.57432590E+03

System 2

Deprotonated PA + H on Cu(100) = -.66710426E+03

ΔE = -0.79095200 eV

All the calculations were done using the same unit cell.

6. Vibrational Mapping of Polymer

The spatial distribution of the inelastic tunneling signal associated with the molecule-substrate vibration, could be illustrated in IETs mapping (Fig. S4b) where the value of d^2I/dV^2 is represented in a color scale as a function of spatial position with a fixed bias at +16 meV. This IETs mapping was taken simultaneously with the topographic image, which is also shown in left panel of Fig. S4a. It allows us to compare the topographic STM image with a vibrational image directly through line profiles across the phenyl rings shown in the bottom panel. First of all, the inelastic features of this molecule-substrate mode show characteristic distributions over 3-4 Å, which is consistence with the previous result. In opposite to the intramolecular modes, which the signal is very localized at the position of the particular bond excited[4, 5], such wide distribution is expected for external molecule-substrate vibration. Second, the center of vibrational signal shifts about 0.8 Å from the center of topographic corrugation (line profiles in bottom panel of Fig. 5B). Since the stretch mode (IETs peak at 16 mV) has its maximal intensity on the mass center of the molecule, the shift we observed suggests the tilting of phenyl rings (Fig. 3B). The tilting angle can be estimated about 12° and is in very good agreement from the tilting angle 16° determined from the DFT calculations.
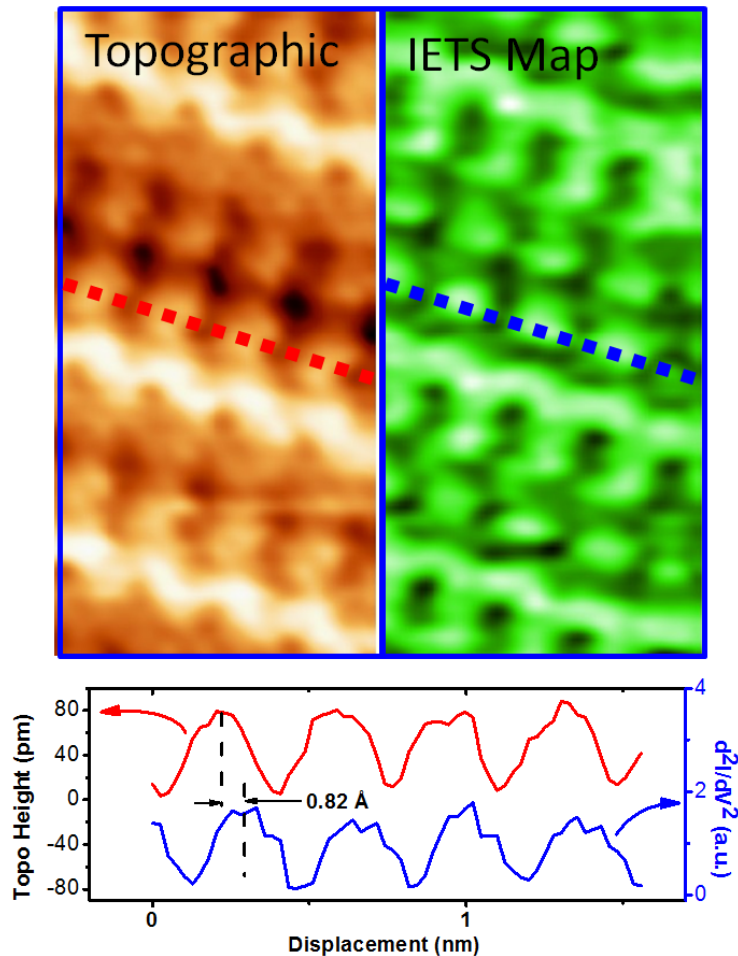
Fig. S5. Spectroscopic spatial imaging of the inelastic channels. Regular constant current STM image (left) and IETs mapping (right). The STM images recorded simultaneously with the vibrational images. The imaged area is 25 Å by 50 Å. d^2I/dV^2 images of the same area recorded at 16 mV.

Reference

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