Supporting Information

Surface-Assisted Dehydrogenative Homocoupling and

Cyclodehydrogenation of Mesityl Groups on Copper Surface

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1. Experimental procedures

The experiments were carried out in a multi-chamber ultrahigh vacuum (UHV) system housing a SPECS variable temperature STM with base pressure of less than 2×10^{-10} mbar. The Cu(110) surface was cleaned by several Ar⁺ sputtering (1.5 keV, 4.8-5.0 μ A, 45 min) and annealing (800 K, 10 min) cycles. 5,15-(dimesityl)porphyrin (DMP) (Frontier Scientific, purity>97%) was evaporated from a Knudsen cell at 473 K on the clean Cu(110) surface held at RT. All STM images were acquired at room temperature with a chemically etched W tip. Positive voltage indicates that the samples were biased positively with respect to the tip.

Density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) ^{1,2} was applied using the PBE generalized-gradient exchange and correlation functional.³ For STM simulations, a plane-wave basis set with a kinetic energy cutoff of 400 eV is used. The van der Waals interaction was considered with the optB86b-vdW method.⁴ Four layers of Cu atoms, separated by a 20Å vacuum region, were employed to model the Cu(110) surface. A 5×10 supercell was adopted to model an isolated molecule adsorbed on the surface and an 8×12 one for two connected molecules. A $1\times1\times1$ k-mesh was adopted for geometry optimizations and STM simulations. In geometry optimizations, all atoms expect those for the bottom two Cu layers were fully relaxed until the residual force per atom was less than 0.02 eV/Å. The STM simulations were performed using the Tersoff-Hamann approximation.⁵

For reaction mechanisms, a plane-wave basis set with a kinetic energy cutoff of 300 eV is used. Core electrons are described by the projected augmented wave method (PAW).^{6,7} Brillouin zones were sampled only at Γ point for the two-layer $p(5\times7)$ surface (the bottom layer Cu atoms were fixed) unit cells with a 15Å vacuum layer. The dispersion correction was calculated using the method of Grimme.^{8,9} The convergence criteria are 1.0×10^{-4} eV for the SCF energy, 1×10^{-3} eV and 0.05 eV/Å for the total energy and the atomic forces, respectively, for structure optimizations. Transition structures have been found using the nudged elastic band (NEB) method,¹⁰ with more than eight equally spaced images along the reaction pathway. The vibrational frequencies and normal modes have been calculated by diagonalization of the mass-weighted force constant matrix, which was obtained by numerically differentiation of analytically calculated forces as implemented in VASP. All reported transition structures are saddle points on the potential energy surface with only one imaginary frequency and all reported minimum energy structures have only real frequencies.

2. The adsorption configuration at room temperature

Figure S1 shows the adsorption configuration of DMP molecules on Cu(110) surface at room temperature. A single DMP molecule is visualized as two protrusions. And one protrusion is much brighter than another for some DMP molecules. Comparison on the two successive STM images show that brighter single spots marked by the arrows could change to normal spots, indicating that brighter single spots are not caused by the crack of DMP molecules. In addition, the observed

brighter single spots are usually at the periphery of self-assembled structures, where the molecule-molecule interaction could be ignored. The corresponding localized electronic distribution is more easily affected by scanning tip, which induce the configuration adjustment of single brighter spots. Hence these spots are resulted from the configuration adjustment induced by scanning tip.



Figure S1. Two STM images of DMP molecules after adsorption on Cu(110) at room temperature recorded successively at same site. The white arrows mark the place where single bright spots change during scanning process. I_t =-0.04nA, V_t =-1400mV.

3. A series of possible structural model of configuration 1

We have calculated a series of possible structural models of configuration 1, as shown in Figure S2. In str1, str2, and str3, the two molecules are connected by single bond, double bond, and triple bond, respectively. The corresponding STM simulating images are given at bellow. We find that there are four bright dots at the connection part of str1, which is not consistent with our experiment observations. There are two bright dots at the connection parts of str2 and str3, and we find that the relatively positions of each dots and the distance between the two dots are in good agreement with our experimental images. However, such calculations show that the str3 configuration is less energy stable due to the triple bond at the connection part. In str4 and str5, a benzene ring was formed between the two molecules. In str4, the two outside carbon atoms of the benzene ring were both saturated by two hydrogen atoms, while in str5, they were both saturated by only one hydrogen atom. Although there are also two bright dots at the connection part of str4, the positions of each dots and the distance between dots are not consistent with our experiments. In the STM simulation of str5, there are no bright dots at the connection part.



Figure S2. A series of possible structural models (str1, str2, str3, str4, and str5) of configuration 1 relaxed on Cu(110) together with the corresponding simulated STM images.

4. The comparing results between STM image and corresponding adsorption geometry.

Figure S3 shows the comparing results between STM image and corresponding adsorption geometry. The core-core distance (see green arrows) and noncoaxial distance (see blue arrows) are measured for configuration 1-3 respectively. The results show the core-core distance (denoted as D in Figure S3) and noncoaxial distance (denoted as d in Figure S3) of the experimental STM image are in good agreement with the theoretical model. The direct overlays of the DFT structures on the STM data show that the STM data of configuration 1-3 matches well with the model.



Figure S3. The comparing results between STM image and corresponding adsorption geometry. (a-c) STM image, adsorption geometry and the overlay of DFT structure on STM image of configuration 1. (d-f) STM image, adsorption geometry and the overlay of DFT structure on STM image of configuration 2. (g-i) STM image,

adsorption geometry and the overlay of DFT structure on STM image of configuration

3.

5. The diffusion energies of the reactants

The calculated energy barriers for the diffusion of one molecule are shown in Figure S4, where red and black line corresponds to the energy of the diffusion along the [001] and [1-10] direction respectively. The results show that the energy barrier along [001] direction is 2.46 eV, and 0.99 eV for along [1-10] direction. Therefore, the energy barrier along [001] direction is about 1.47 eV higher than that along [1-10] direction.



Figure S4. The energy barriers for the diffusion of one molecule along [001] and [1-10] direction.

6. The detailed structures and imaginary frequences of the dehydrogenative

homocoupling reaction

Figure S5 shows the structures for the simplified reactant molecules lying along different directions on the surface. It is found that the physical adsorbed simplified molecules lying along the [1-10] direction is 0.18 eV more favored than along the [001] direction.



Figure S5. Structures of the simplified molecules on the Cu surface along the [1-10] and [001] direction. H, C and Cu atoms are shown in small white, gray and cupric, respectively.

Figure S6 shows the structures of the simplified molecules, reaction intermediates and the transition states on the Cu surface, the labels of each figure correspond to the Fig 3b in the text. In order to facilitates the reading of the figures, the reactant part of the molecules are shown enlarge in the middle of the figure. The bond distances are given to show the detailed structure. The imaginary frequencies of the transition state structures are calculated and shown in the figure.



t3(along [1-10] direction)

(b)



Figure S6. Structures of the simplified molecules, reaction intermediates and the transition states on the Cu surface, the labels of each figure correspond to the Fig 3b in the text. The bond distances are given in pm, and the imaginary frequencies (if) of the transition states structures are given in the box. H, C and Cu atoms are shown in small white, gray and cupric, respectively.

7. Polymerization chain cross the steps of Cu(110) surface

Figure S7 gives the case that a chain spans three consecutive steps on the surface.

The height profile in Figure S7(f) shows that the scanning area contains three copper atomic steps with the height of 1.3Å. Two connection sites across the steps highlighted by the dotted rectangles are examined by high resolution STM in Figures S7(b-c). The declining trend of the height in Figure S7(d-e) suggests that the DMP molecule across the steps is reclining between two steps, further declaring there is no crack at the edge of step.



Figure S7. Polymerization chain cross the steps of Cu (110) surface. (a) The largescale STM image. I_t=-0.05 nA, V_t=-1000 mV. (b-c) The high resolution STM images

of dotted rectangles in (a). I_t =-0.05 nA, V_t =-1000 mV. (d-e) The height profiles across the blue arrows in (b-c). (f) The height profiles across the white arrow in (a).

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