

Supporting Information

Lattice-Directed Formation of Covalent and Organometallic Molecular Wires by Terminal Alkynes on Ag Surfaces

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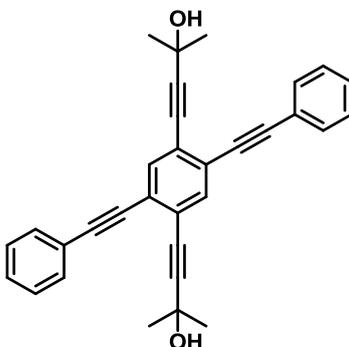
Toulouse, France

1. Preparation of 2,5-diethynyl-1,4-bis(phenylethynyl)benzene (DEBPB)

General methods

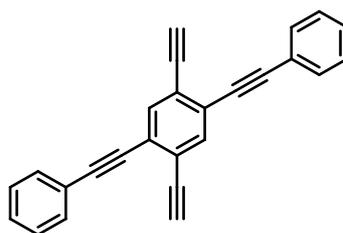
¹H and ¹³C NMR spectra were obtained on BRUKER AVANCE III 400 spectrometers. All ¹³C NMR spectra were recorded with the simultaneous decoupling of ¹H nuclei. Chemical shifts are reported in parts per million (ppm) with TMS (0 ppm) as the reference for ¹H NMR spectra and CDCl₃ (77.02 ppm) as reference for ¹³C NMR spectra. Tetrahydrofuran, triethylamine and toluene were distilled over sodium benzophenone, calcium hydride, and sodium under N₂ atmosphere, respectively. 4,4'-(2,5-Dibromo-1,4-phenylene)bis(2-methylbut-3-yn-2-ol) and trimethyl(phenylethynyl)silane were synthesized according to previously reported procedures.^{1,2}

Preparation of 4,4'-(2,5-bis(phenylethynyl)-1,4-phenylene)bis(2-methylbut-3-yn-2-ol)



A Schlenk tube containing 4,4'-(2,5-dibromo-1,4-phenylene)bis(2-methylbut-3-yn-2-ol) (190 mg, 0.47 mmol), CuI (90 mg, 0.47mmol), KF·2H₂O (223 mg, 2.37mmol), and Pd(PPh₃)₂Cl₂ (10 mg, 0.02 mmol) was evacuated and back-filled with nitrogen three times. Degassed tetrahydrofuran (5 mL), triethylamine (5 mL), acetonitrile (1 mL) and trimethyl(phenylethynyl)silane (248 mg, 1.43 mmol) were added into the tube under nitrogen atmosphere. The flask was then sealed and the mixture was stirred at 80 °C overnight. After cooling to rt, the mixture was washed with saturated NH₄Cl (aq.) solution and then brine. The organic layer was dried over anhydrous Na₂SO₄ and then the solvents were removed *in vacuo*. Column chromatography (petroleum ether/ethyl acetate=6:1, v/v) was performed with the light brown residue and gave 162 mg (77%) of the product as a light brown solid. ¹H NMR (400 MHz, CDCl₃): δ 7.63 (s, 2H), 7.56 (m, 4H), 7.37 (m, 6H), 2.04 (s, 2H), 1.65 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 135.0, 131.7, 128.8, 128.5, 125.4, 122.8, 99.7, 96.2, 87.2, 80.1, 66.8, 31.4.

Preparation of 2,5-diethynyl-1,4-bis(phenylethynyl)benzene (DEBPB)



A Schlenk tube containing 4,4'-(2,5-bis(phenylethynyl)-1,4-phenylene)-bis(2-methylbut-3-yn-2-ol) (162 mg, 0.37 mmol) and KOH (82 mg, 1.46 mmol) was evacuated and back-filled with nitrogen three times. Toluene (5 mL) was added into the tube before the tube was sealed. The mixture was then stirred at 80 °C for 60 min. After cooling to rt, the mixture was washed with saturated NH₄Cl (aq.) solution and then brine. The organic layer was dried

over anhydrous Na_2SO_4 and then the solvents were removed *in vacuo*. Column chromatography (petroleum ether/dichloromethane=6:1, v/v) was performed with the light brown residue and gave 100 mg (84%) of the product as a light yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 2H), 7.56 (m, 4H), 7.37 (m, 6H), 3.45 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 135.6, 131.9, 138.9, 138.4, 125.8, 124.8, 122.7, 95.7, 86.9, 83.1, 81.0.

2. The Creation of a CO-Modified Tip

The CO-modified tip was obtained by following the method reported by Lee and coworkers.³ Figure S1 showed the process to create a CO-modified tip on Ag(110). With a metal tip, CO molecules adsorbed on Ag(110) were imaged as dark spots as marked by black and white arrows in Figure S1a. After the successful creation of CO-modified tip by picking up the CO marked by black arrow in Figure S1a, the two left CO molecules marked by white arrows in Figure S1b turned into bright spots. The similar conversion in the imaging of CO molecules had been generally observed in other systems,^{4, 5} which could serve as a sign of the successful creation of a CO-modified tip. Meanwhile, the resolution of the STM image of organometallic chains was evidently improved by using a CO-modified tip as shown in Figure S1b

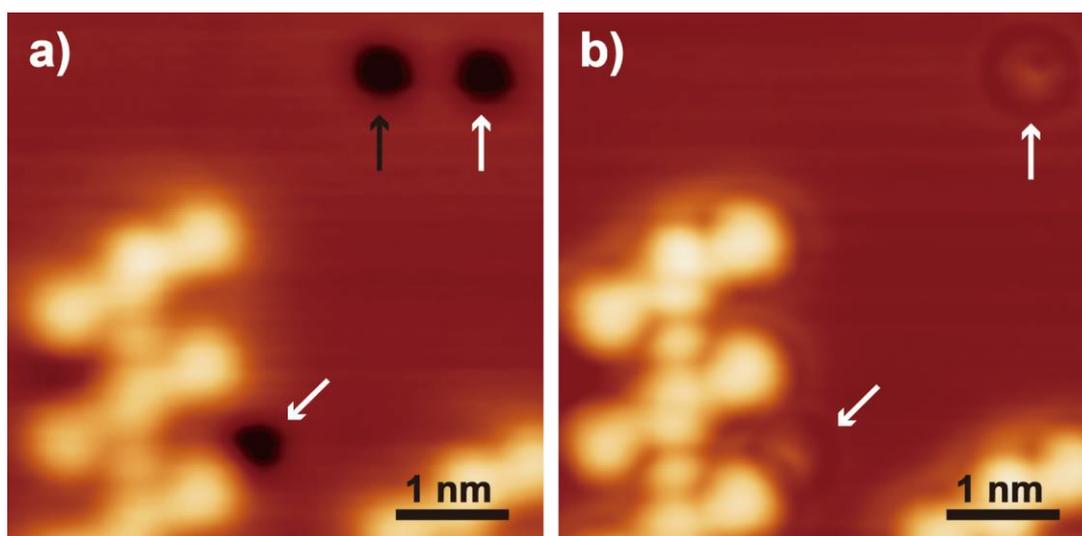


Figure S1. (a) STM image of organometallic chains and adsorbed CO molecules on Ag(110) obtained by using a metal tip (0.01 V, 100 pA). The CO molecules are marked by black and white arrows. (b) STM image of the same area obtained by using a CO-modified tip created by picking up the CO marked by black arrow in (a) (0.05 V, 100 pA). The adsorbed CO molecules are marked by white arrows.

3. Further Conversions of Organometallic Chains on Ag(110) at Higher Annealing Temperatures

Further annealing at about 400 K of Ag(110) substrate gave rise to some compressed or inflected segments in the chains as highlighted by dashed circles in Figure S2a. By detailed investigations, all these segments could be classified into four typical types, and examples of each type were marked as “I”, “II”, “III” and “IV” in Figure S2a. High-resolution STM images of these four types of structures (Figure S2b-e) unexceptionally showed direct connections between molecules without round dots, which suggested the formation of covalent bonds between molecules in these structures. Yet, none of these structures was

Glaser Coupling product of DEBPB molecules. To be specific, in the case of Structure I and II (Figure S2b and S2c), the backbone of molecule in the segments were apparently bent comparing to DEBPB monomers as well as molecules in Glaser coupled covalent chains on Ag(111), indicating that some chemical conversions had taken place within the molecular backbones in Structure I and II. These oligomers of molecules with chemical converted backbones might result from Bergman Cyclization and the following radical polymerization of the molecules due to the existence of alkynyls as the *ortho* substituents at the arene next to the terminal alkynyls in DEBPB molecules.⁶ On the other hand, as for Structure III and IV, high-resolution STM images (Figure S2d and S2e) showed an invariant molecular backbone as DEBPB monomers which demonstrated the maintenance of the chemical structure of the molecules in Structure III and IV. However, the distances between centers of adjacent molecules as marked by white arrows in Figure S2d and S2e were measured as 0.73 ± 0.05 nm and 0.82 ± 0.04 nm, respectively, for Structure III and IV. Both of these two distances were obviously shorter than that between centers of two Glaser coupled DEBPB molecules, that is, 0.91 nm, which illustrated that molecules in Structure III and IV did not connect with each other through Glaser Coupling. In addition, the kinks that Structure III and IV brought about also suggested bonding modes other than Glaser Coupling between molecules, since Glaser Coupling would lead to straight covalent connections. These compressed and kinked connections in Structure III and IV might result from the bonding between partially reduced terminal alkynyl groups.^{7, 8} Therefore, none of these structures was Glaser Coupling product of DEBPB molecules: either molecular backbone structure or connecting method showed difference. Even at higher annealing temperatures, say, 450 K, no Glaser Coupling product

but only increased segments of structure I, II, III and IV, as well as remained organometallic chains were observed.

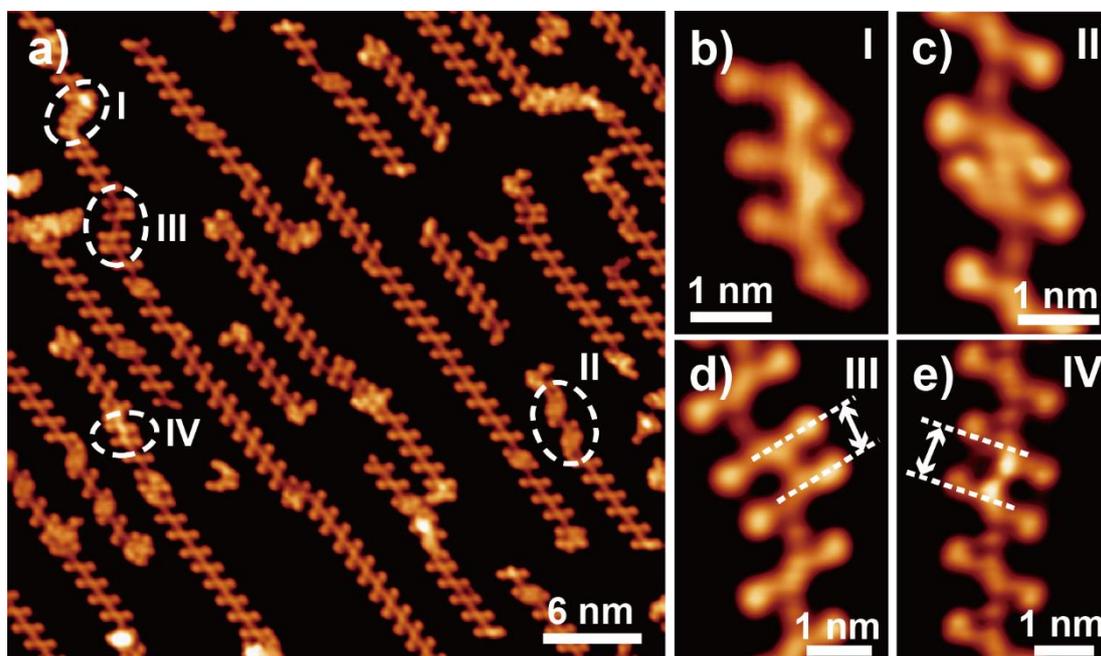


Figure S2. (a) STM image of organometallic chains with inflected or compressed segments on Ag(110) after annealing at about 400 K (0.01 V, 160 pA). Four typical types of structures, “I”, “II”, “III” and “IV” are marked and highlighted by white dashed circles. High-resolution STM images of (b) Structure I (0.01V, 400pA, constant height mode), (c) Structure II (0.01V, 110pA, constant height mode), (d) Structure III (0.01V, 110pA, constant height mode), and (e) Structure IV (0.01V, 110pA, constant height mode). The distances measured between centers of adjacent molecules in Structure III and IV are highlighted by white arrows in (d) and (e).

4. Overview STM Images of Organometallic Chains Formed on Ag(100)

After the thermal treatment, a low coverage of organometallic chains was observed on Ag(100) due to desorption of the molecules during the annealing process.

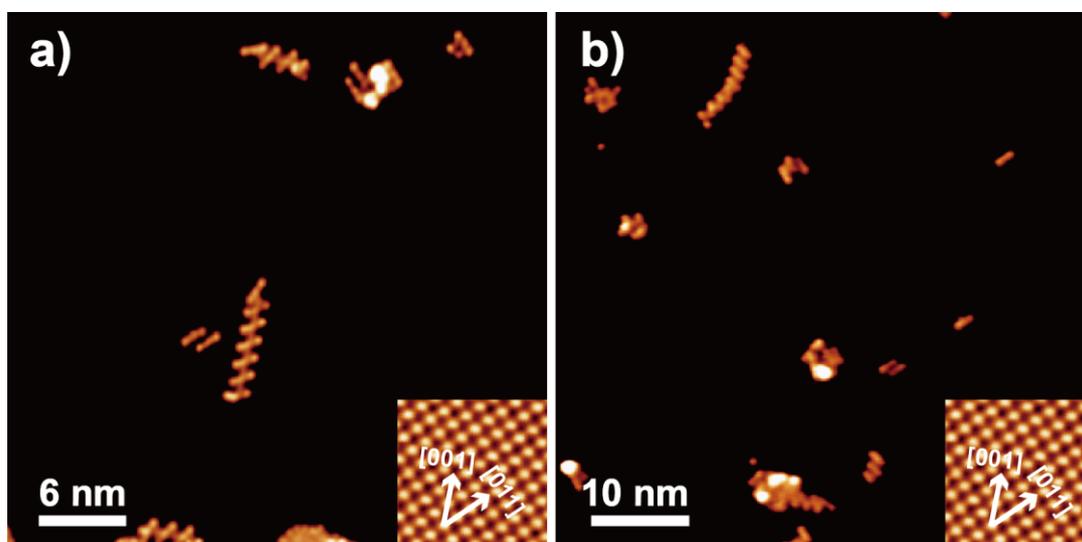


Figure S3. STM images of the produced organometallic chains on Ag(100) after annealing at about 320 K. Imaging conditions: (a) 0.01 V, 200 pA; (b) 0.05 V, 100 pA. Insets, high-resolution STM images of the Ag(100) surface lattice (0.01 V, 200 pA).

5. Statistics on the Productivity of Reaction Products on Ag(111), Ag(110) and Ag(100)

Here is how the productivity of each product on Ag(111), Ag(110) and Ag(100) was figured out. Firstly, the total number of DEBPB molecules was counted out from STM images of the annealed samples. Given that both covalent and organometallic connections required two terminating alkynyls which were just the number of terminating alkynyls every DEBPB monomer got, the number of connections in specific type could be taken as the number of molecules taking part in the corresponding reaction. Therefore, the number of Glaser coupled connections was counted and was taken as the number of molecules participating in Glaser Coupling. In the same way, the number of organometallic connections was counted and was taken as the number of molecules reacting with Ag adatoms. By

subtracting the number of molecules taking part in Glaser Coupling or organometallic reaction from the total number, what left was the number of molecules that didn't completely react (the remained monomers or the ones at the end of chains) or participated in other side reactions. Such statistics were conducted on over 1000 molecules on Ag(111) and Ag(110), respectively, and over 100 molecules on Ag(100) due to the low coverage after being annealed at about 320-350 K. As a result, on Ag(111), the productivity of Glaser Coupling product was 70%, while the productivity of organometallic species was 9%. On Ag(110) and Ag(100), the productivity of organometallic nanostructures was 88% and 42%, respectively, and no Glaser Coupling product was found.

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