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Supplementary Materials for

Bottom-Up Synthesis of Metalated Carbyne

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Methods

STM characterization and sample preparation. All the STM experiments were carried out *in situ* in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature “Aarhus-type” STM^{1,2}, a molecular evaporator and standard facilities for sample preparation. All of the samples are prepared in UHV chambers with base pressures $\sim 1 \times 10^{-10}$ mbar. After the Cu(110) substrate was carefully cleaned with repeated Ar⁺ sputtering and annealing processes under UHV conditions, the ethyne molecules were dosed into the preparation chamber from a leak valve with a partial pressure of 1×10^{-8} mbar for 5-20 minutes (depending on the desired surface coverage), while most importantly, keeping the substrate temperature at ~ 450 K. The STM measurements were carried out in a typical temperature range of 100 K~150 K in constant current mode. Typical scanning conditions: $I_t = 0.5\sim 1.0$ nA, $V_t = -1.0\sim 2.0$ V.

DFT calculation. All calculations were performed in the framework of density functional theory (DFT) by using the Vienna Ab Initio Simulation Package (VASP)^{3,4}. We have used the projector augmented wave method^{5,6}, and the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional⁷, and van der

Waals (vdW) interactions were included using Grimme's semiempirical method (DFT-D2)⁸. The atomic structure was relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all atoms except the two bottom layers were ≤ 0.01 eV/Å.

X-ray photoelectron spectroscopy. Photoemission spectroscopy experiments were performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. This system comprises four ultrahigh vacuum (UHV) chambers including analysis chamber, preparation chamber, molecular beam epitaxy (MBE) chamber, and a radial distribution chamber, whose base pressures are 7×10^{-11} , 1×10^{-10} , 5×10^{-10} and 2×10^{-11} mbar, respectively. In addition, a quick sample load-lock system is attached to the radial distribution chamber. All of the core level spectra including C 1s and Cu 2p were recorded with a VG Scienta R4000 analyzer using a monochromatic Al K α X-ray source. The peak fitting was performed using the XPS Peak 41 program with Gaussian functions after subtraction of a Shirley background. The photon energies were calibrated and referenced to the Cu binding energy of a sputter-cleaned Cu substrate. Before every scan of the C 1s spectra, we will also measure the Cu binding energy of the Cu substrate for calibration.

***In-situ* STM imaging and X-ray photoelectron spectroscopy.** To further verify the experimental observations, we have also performed *in-situ* STM imaging and X-ray photoelectron spectroscopy experiments at Hubei University in Wuhan, China. This system comprises two ultrahigh vacuum (UHV) chambers. The analysis techniques include X-ray photoemission spectroscopy, Low energy electron diffraction, and Scanning tunneling microscopy. All core level spectra including C 1s and Cu 2p were recorded with a SPECS Phoibos 150 analyzer using a dual anode (Al/Mg) Al K α X-ray source.

Constant height non-contact AFM imaging. Sample analysis was performed in situ with a commercial low temperature SPM (Omicron GmbH) at 5.5 K. Non-contact AFM measurements have been performed with a tungsten tip attached to a tuning fork sensor. The performance of the tip was optimized by picking up a CO molecule from the copper surface. The sensor has been driven close to its resonance frequency (~ 23530 Hz) with a constant amplitude of approximately 70 pm. The shift in the resonance frequency of the tuning fork (with the attached CO-functionalized tip) has been recorded in constant height mode (Omicron Matrix electronics and HF2Li PLL by Zurich Instruments).

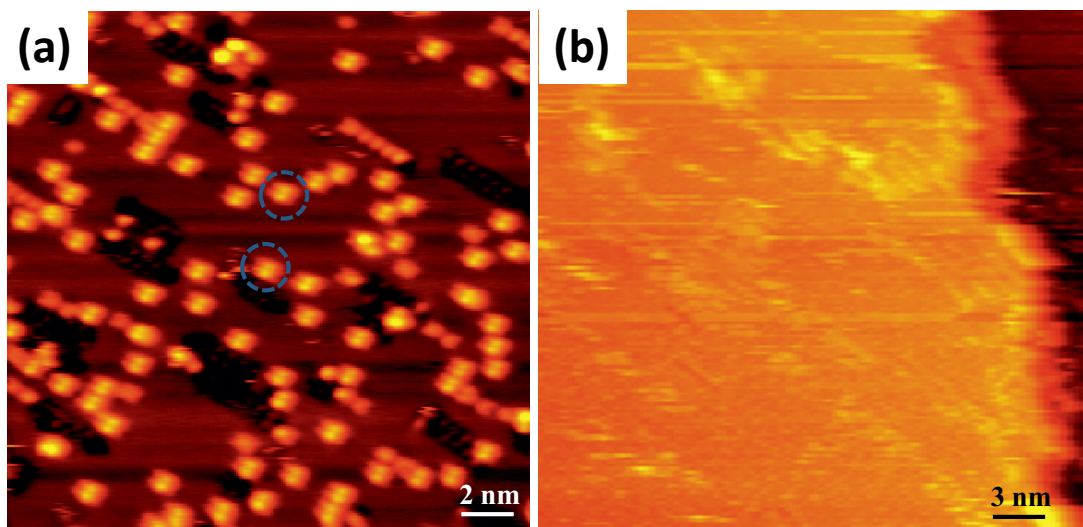


Fig. S1. STM images obtained after deposition of ethyne on Cu(110) at ~ 220 K (a) and further annealing the sample to ~ 330 K (b). The bright protrusions highlighted by blue dashed circles in (a) are supposed to be related to benzene on Cu(110). They desorb from the surface after annealing the sample to ~ 330 K.

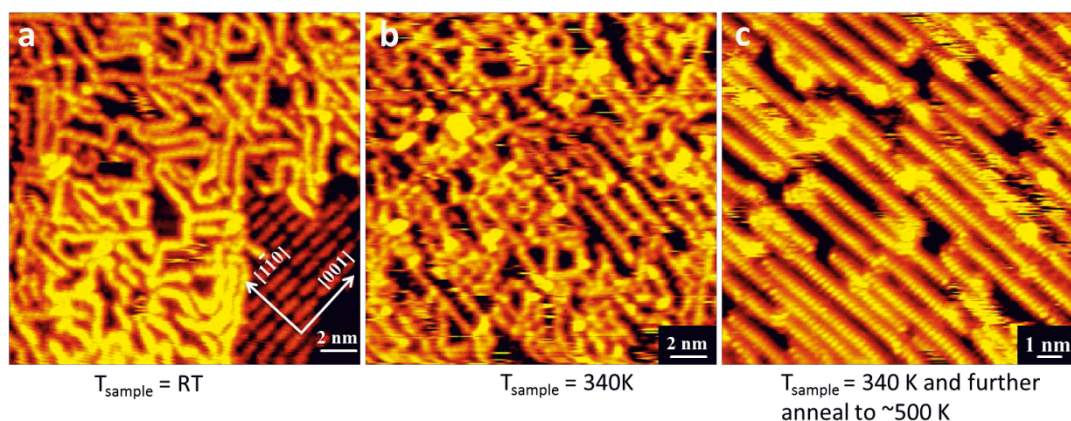


Fig. S2. Some other structures that are formed under different experimental conditions. (a) Dosing ethyne while keeping the substrate temperature at room temperature. (b) Dosing ethyne while keeping the substrate temperature at 340 K. (c) Dosing ethyne while keeping the substrate temperature at 340 K followed by annealing the sample to 500 K. The structure in (c) is polyacetylene rather than carbyne, as confirmed by nc-AFM imaging [to be published elsewhere].

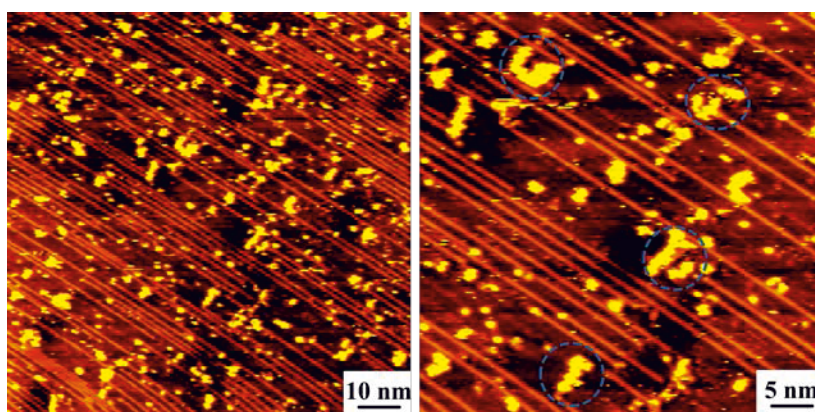


Fig. S3. Overview STM image of a typical metalated carbyne on Cu(110) sample. The dashed blue circles indicate undetermined byproducts which should be related to the C1 peak of Figure 2d.

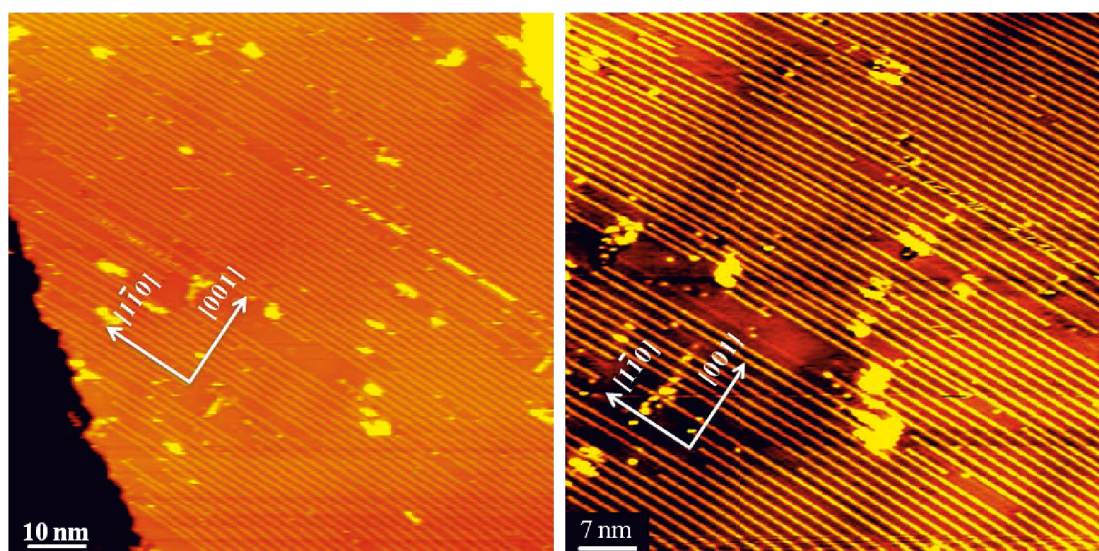


Fig. S4. STM images showing the formation of metalated carbyne extending into the submicron scale at high surface coverages.

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