Supplementary information for

Atomic-Scale Visualization of Stepwise Growth Mechanism of Metal-Alkynyl Networks on Surfaces

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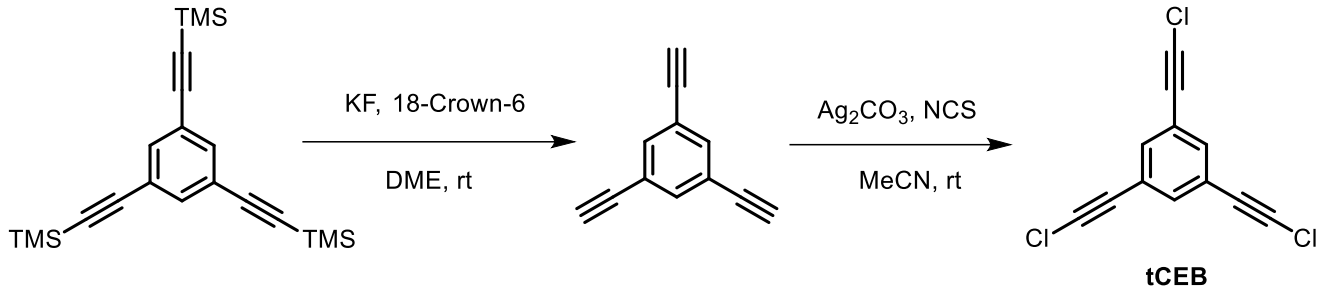
Contents:

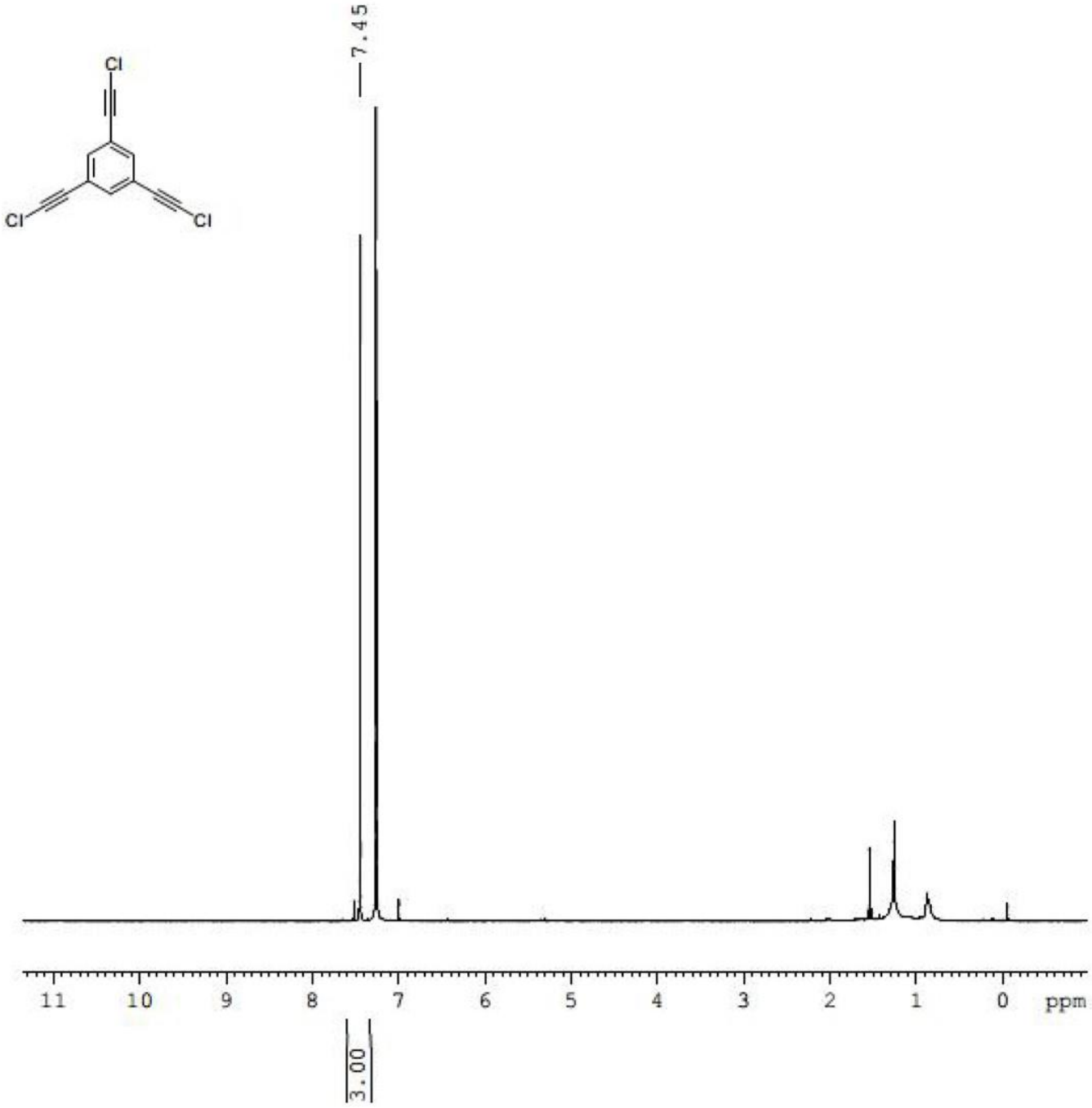
1. Synthesis of organic molecule (tCEB)



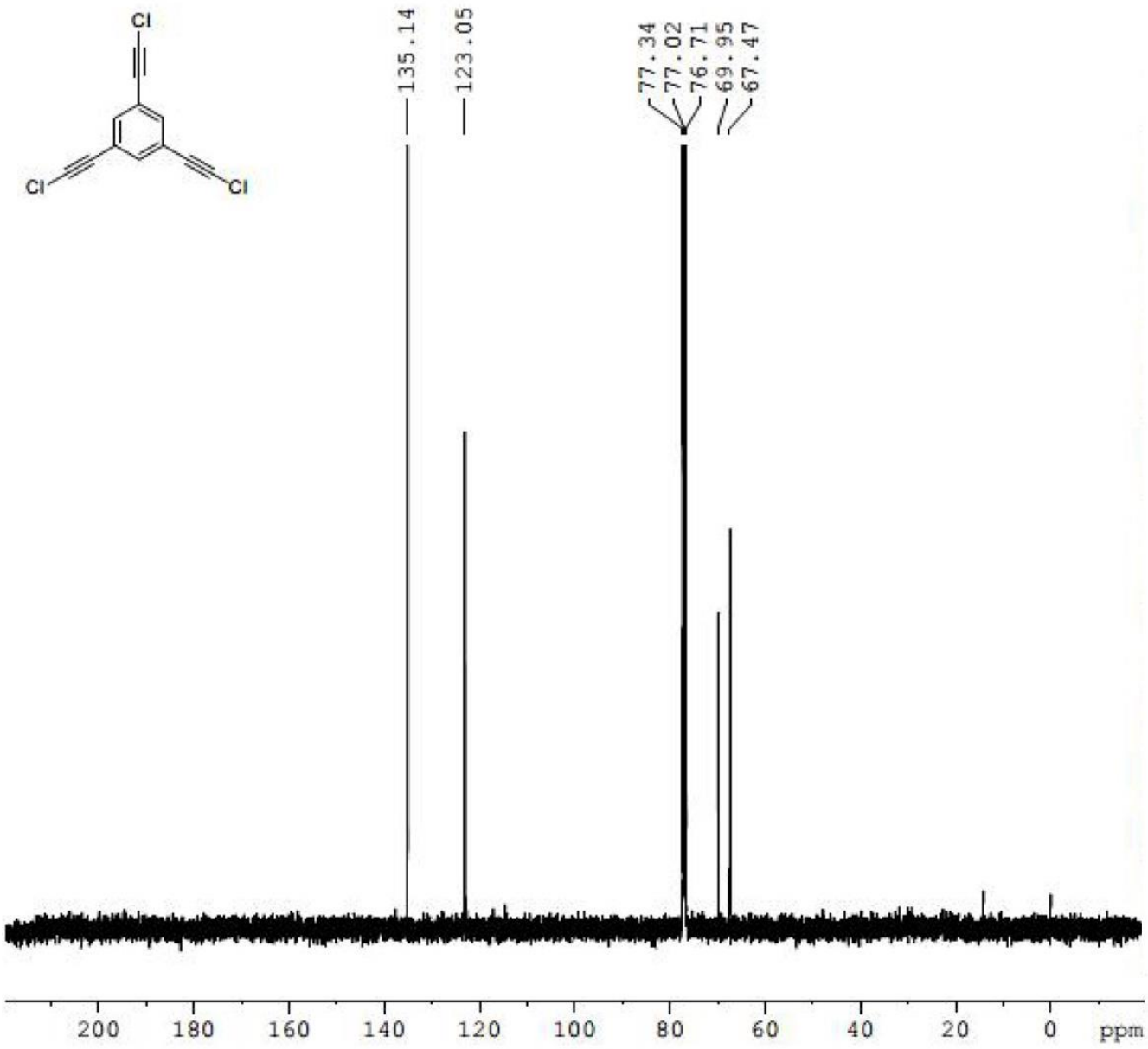
tCEB

1,3,5-tris((trimethylsilyl)ethynyl)benzene (100 mg, 0.27 mmol), ethylene glycol dimethyl ether (20 mL), potassium fluoride (270 mg, 5.5 mmol) and 18-crown-6 (10 mg) were mixed and stirred at room temperature for 3h, and the reaction progress was monitored by TLC. After the reaction completed, the mixture was washed with saturated brine, and extracted with dichloromethane. After dried over organic phase with $MgSO_4$ (anhydrous), the solvent was removed in vacuum. The next reaction was performed immediately without purification and separation. The obtained reaction mixture was mixed with acetonitrile, silver carbonate (60 mg, 0.22 mmol), tetrabutylammonium fluoride (15 mg) and N-chlorosuccinimide (390 mg, 2.2 mmol), and stirred for 12 h at room temperature. Then, the mixture was washed with saturated brine, extracted with dichloromethane, dried over organic phase with $MgSO_4$ (anhydrous), and then column chromatography was performed by silica gel (eluent: PE) to offord 51 mg of a white solid product with a yield of 75%. **^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C)** δ 7.50 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 135.1, 123.0, 70.0, 67.5 ppm; **HRMS (EI, TOF)** calcd for $C_{12}H_3Cl_3^+$ $[M]^+$: 251.9300, found: 251.9302; **MP**: 84.7-86.6 °C.

^{1}H NMR of 1,3,5-tris(chloroethynyl)benzene



^{13}C NMR of 1,3,5-tris(chloroethynyl)benzene



2. General procedure for the STM experiment

The STM measurements were carried out at 77 K in constant-current mode. The Ag(111) and Au(111) (from MaTecK) were cleaned by repeated Ar^+ ion sputtering and annealing cycles (1.1 keV, 750 K). The 1,3,5-tris(chloroethynyl)benzene was thermally evaporated from a leak valve held at 293 K. The molecule was thoroughly degassed before installed on the preparation chamber. Metal substrates were kept at low temperatures (150 K) during the evaporation and were subsequently heated to the indicated temperatures to initiate reactions. The STM images were processed and exported using Gwyddion software.

3. General procedure for the density of functional theory calculations

The calculation models were constructed by the Materials Studio 8.0 and the image of relaxed models were processed and exported using the Materials Studio 8.0.

The calculations were carried out in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).[1,2] The projector augmented wave method was used to describe the interaction between ions and electrons.[3,4] We used the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) formulism to treat exchange-correlation interaction,[5] and van der Waals (vdW) interactions were considered by using the DFT-D3 developed by Grimme.[6] The structures were relaxed until the forces on all unconstrained atoms were ≤ 0.1 eV/Å. All surfaces were modeled by two layered slabs separated by at least 10 Å of vacuum. Calculated lattice constants of 4.11 Å for Au and 4.14 Å for Ag were used. All calculations were done with a 1×1×1 k-point sampling and a 400 eV kinetic energy cutoff. The Cl···H interactions were studied by Atoms-In-Molecules (AIM) analysis.

4. Experimental and DFT calculation results

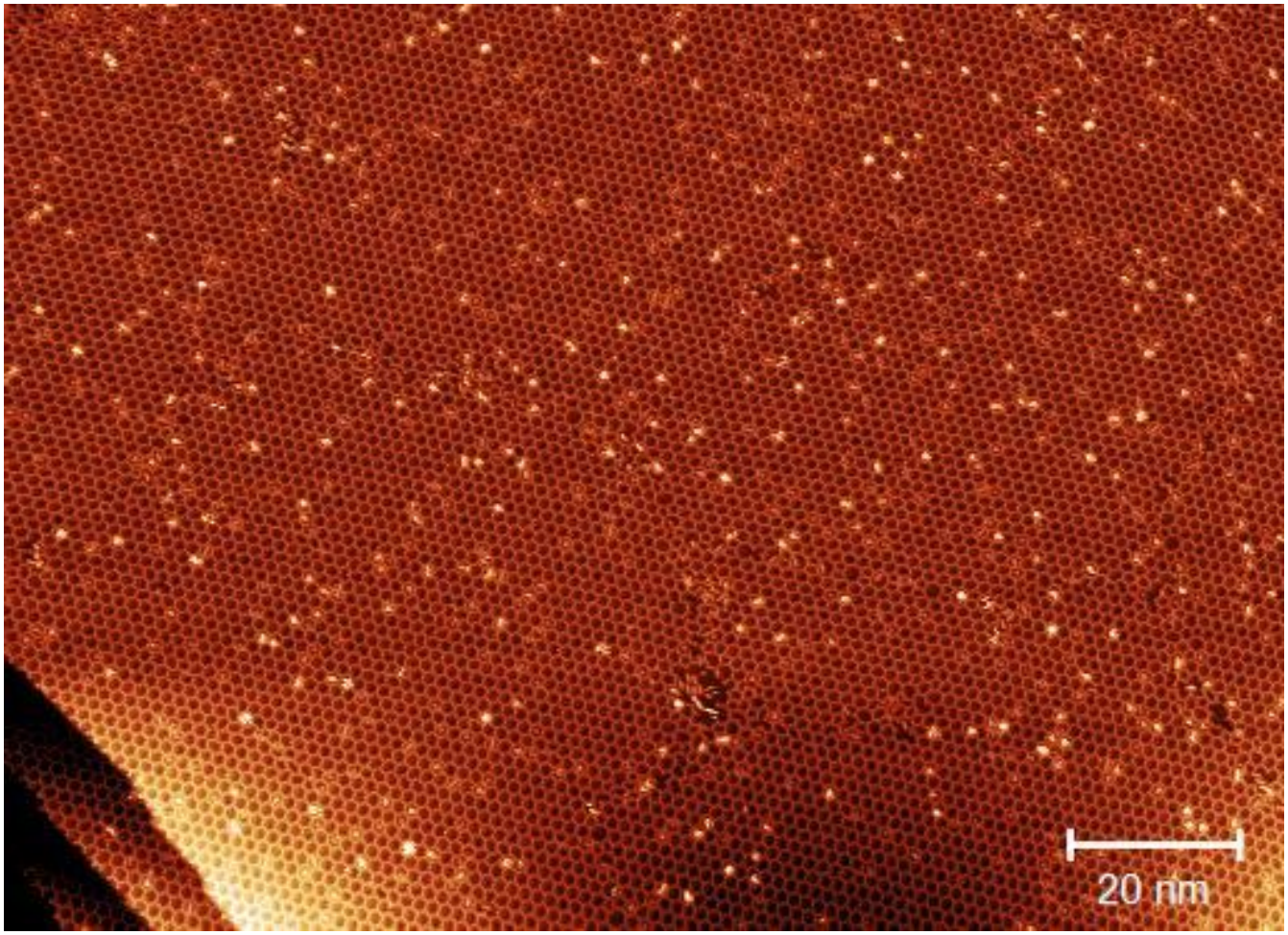


Figure S1. Large-scale honeycomb Ag-alkynyl networks formed on Ag(111) surface after annealed the sample at 393 K. Scanning parameters: U = -1.0 V, I = 0.1 nA.

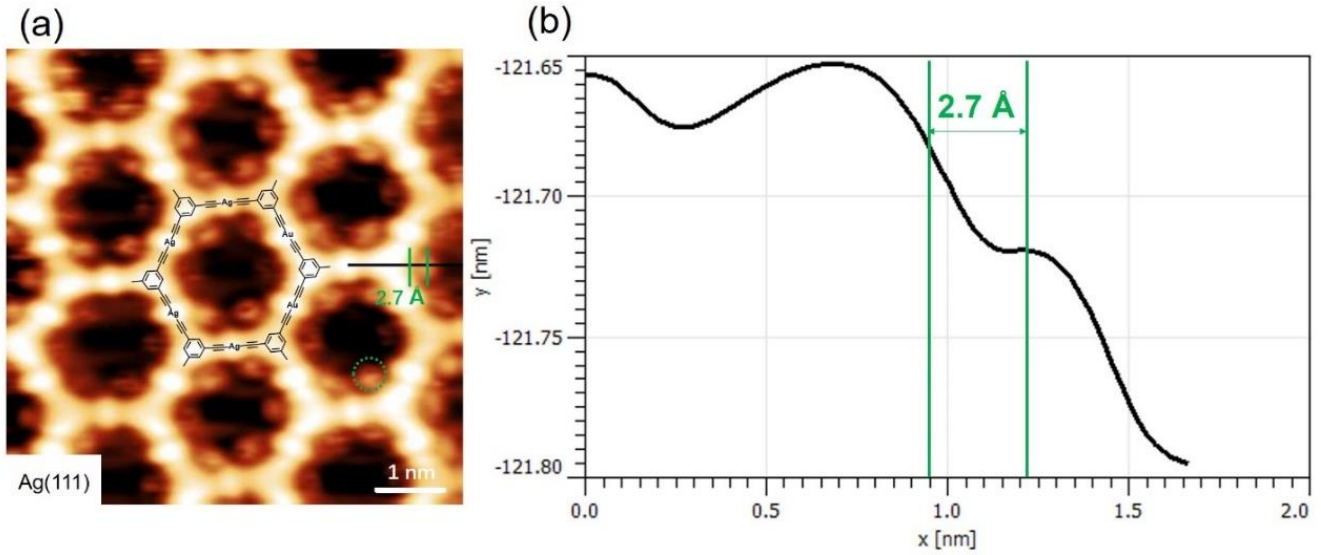


Figure S2. (a) Honeycomb Ag-alkynyl networks on Ag(111) surface. Scanning parameters: *U* = -1.0 V, *I* = 0.1 nA. The black line marks the line profile. (b) Length measurement of Cl···H in the line profile.

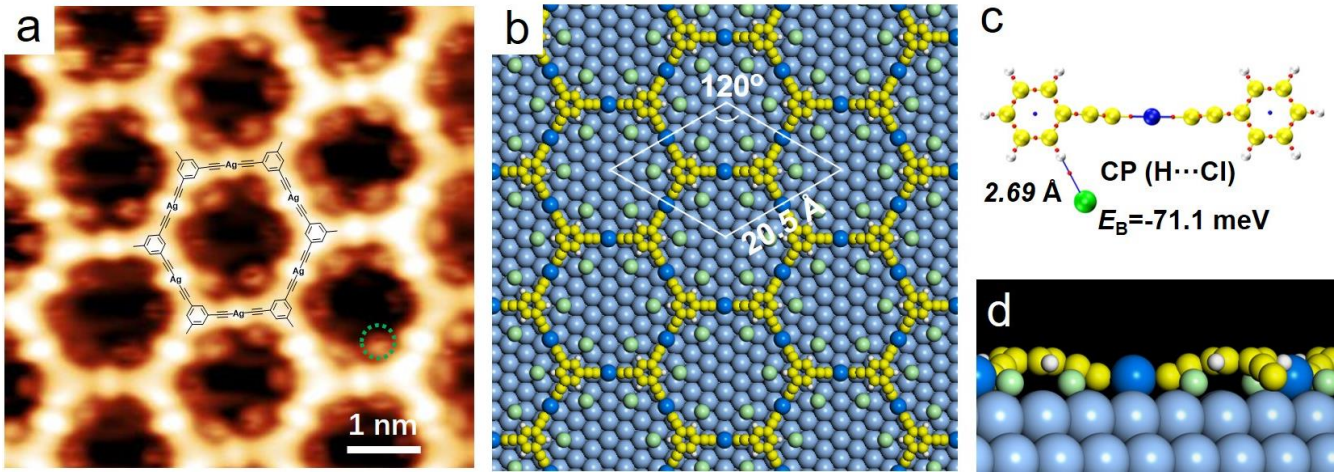


Figure S3. (a) STM image of the honeycomb Ag-alkynyl networks with detached chlorine atoms. Scanning parameters: *U* = -1.0 V, *I* = 0.1 nA. (b) DFT-calculated structure of the honeycomb Ag-alkynyl networks with detached chlorine atoms. (c) AIM analysis of the bond energy of Cl···H interaction, E_b = -71.1 meV. (d) Side view of the DFT-calculated structure.

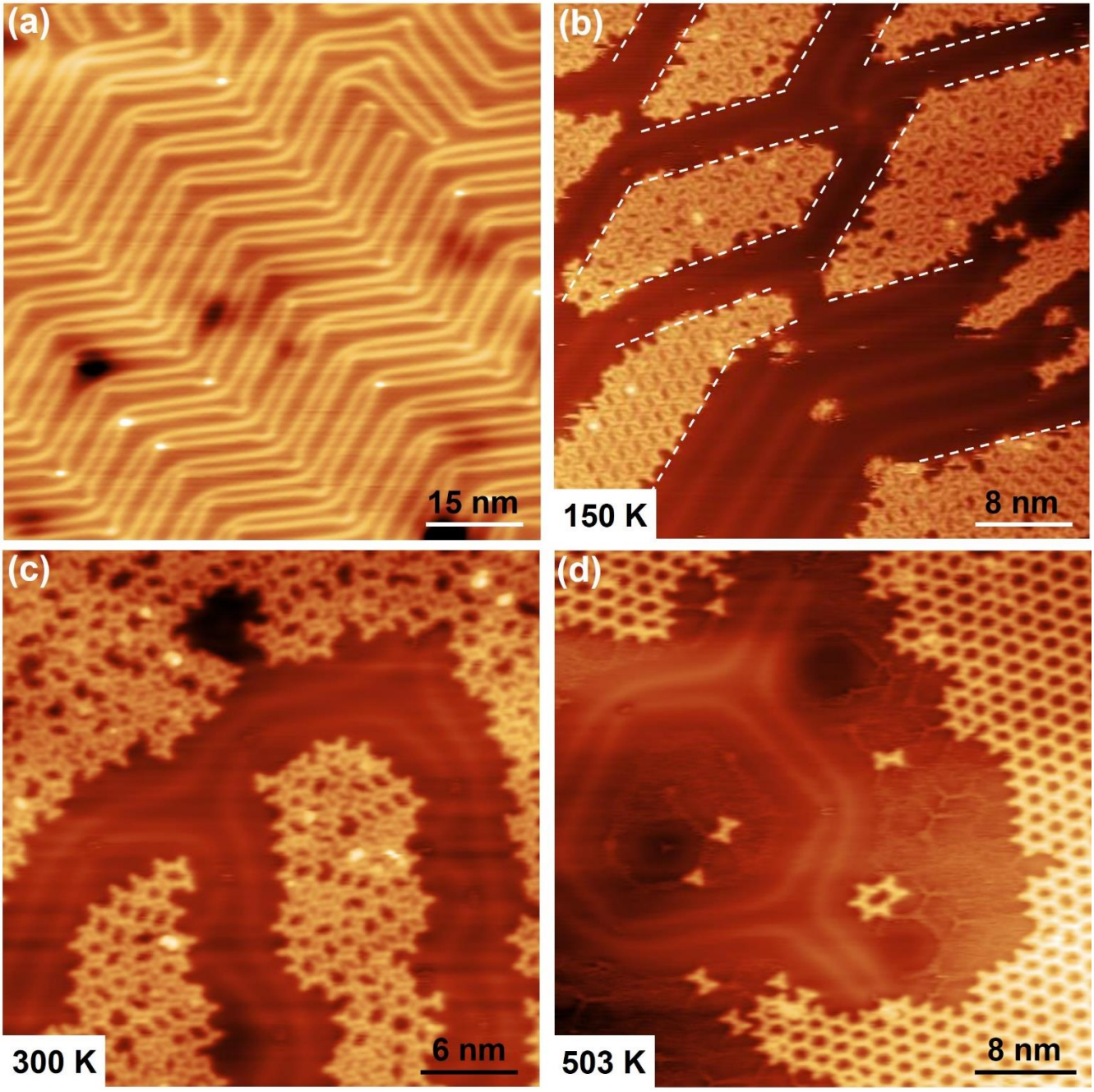


Figure S4. (a) Herringbone reconstruction of a clean Au(111) surface. (b) Au(111) herringbone reconstruction after deposition of tCEB on Au(111) surface at 150 K. (c) Au(111) herringbone reconstruction is lifted after annealing the sample to 300 K. (d) Au(111) herringbone reconstruction is not restored after annealing the sample to 503 K. Scanning parameters: U = -1.0 V, I = 0.1 nA.

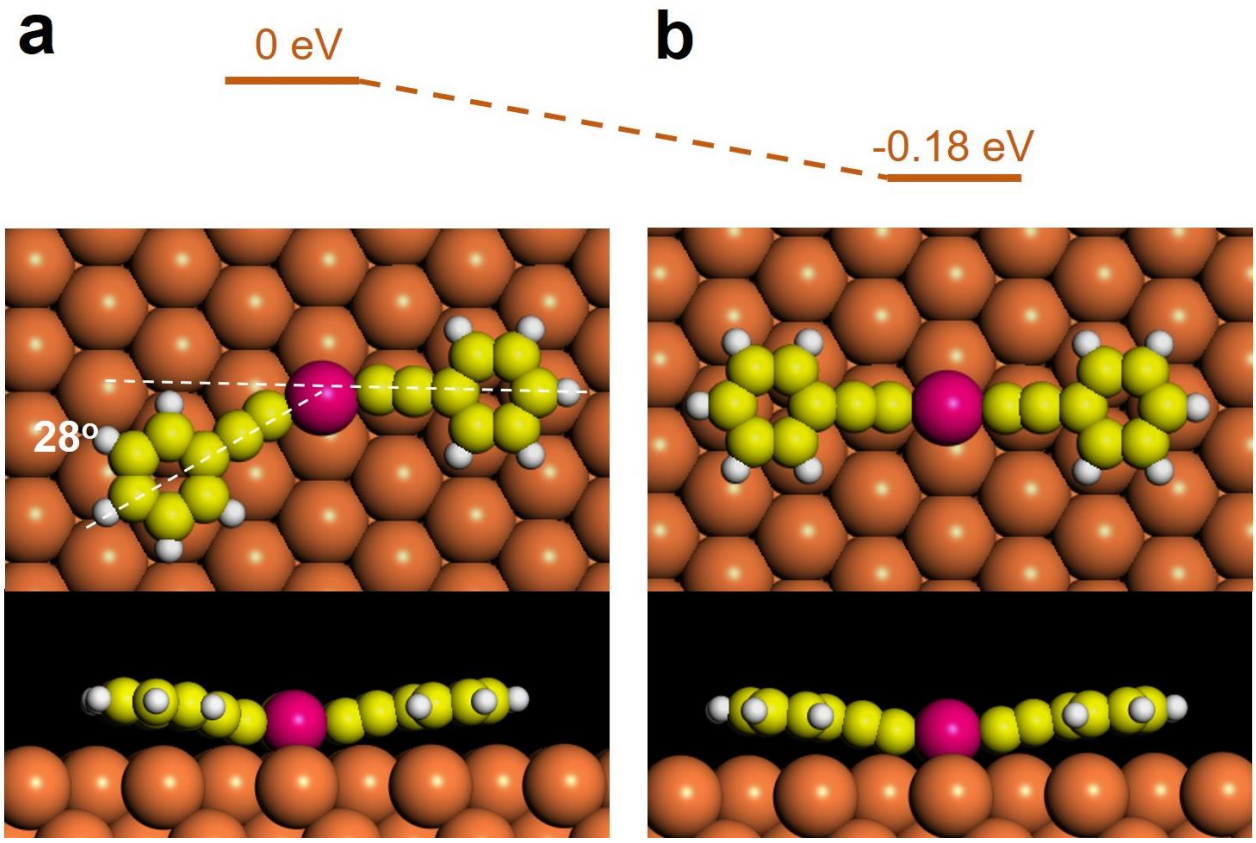


Figure S5. DFT-relaxed structures of (a) nonlinear alkynyl-Au-alkynyl bonds and (b) linear alkynyl-Au-alkynyl bonds. $\Delta E = E_b - E_a$ = -0.18 eV.

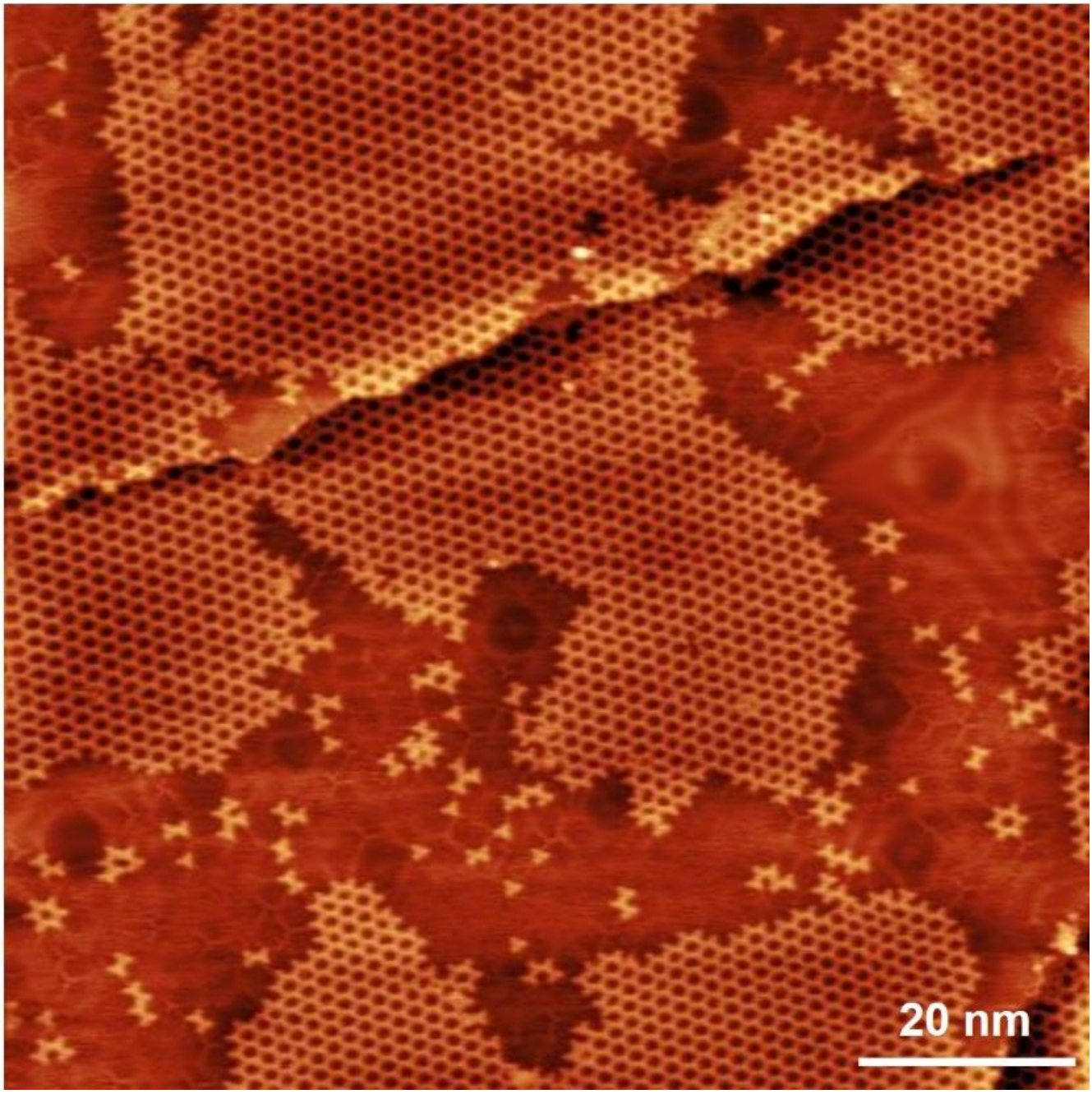


Figure S6. STM image of honeycomb Au-alkynyl networks on Au(111) surface. Scanning parameters: *U* = -1.0 V, *I* = 0.1 nA.

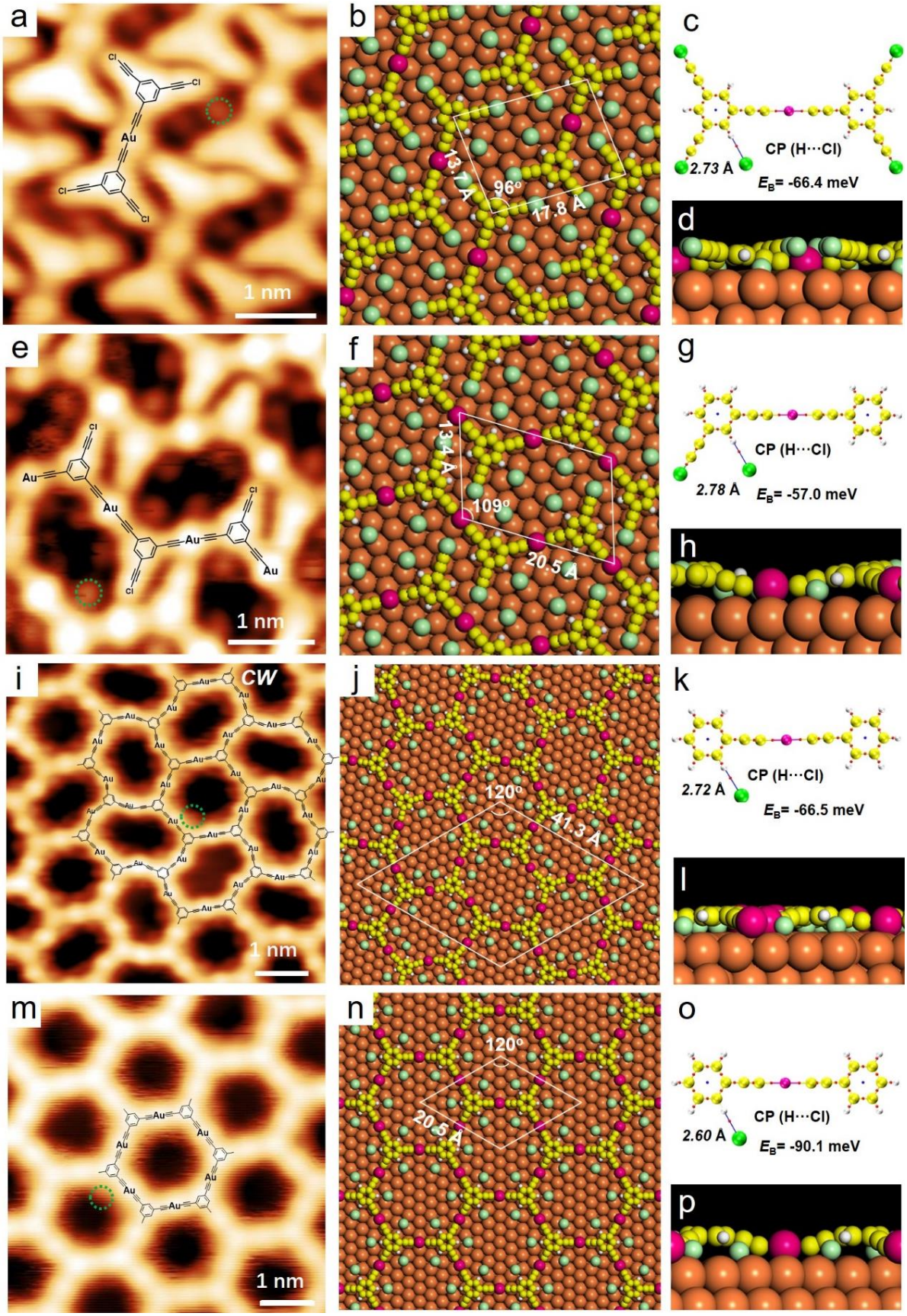


Figure S7. (a, e, i, m) STM images of the Au-alkynyl structures with detached chlorine atoms. Scanning parameters: *U* = -1.0 V, *I* = 0.1 nA. (b, f, j, n) DFT-calculated structures of the Au-alkynyl structures with detached chlorine atoms. (c, g, k, o) AIM analysis of the bond energy of Cl···H interactions. (d, h, l, p) Side views of the DFT-calculated structures.

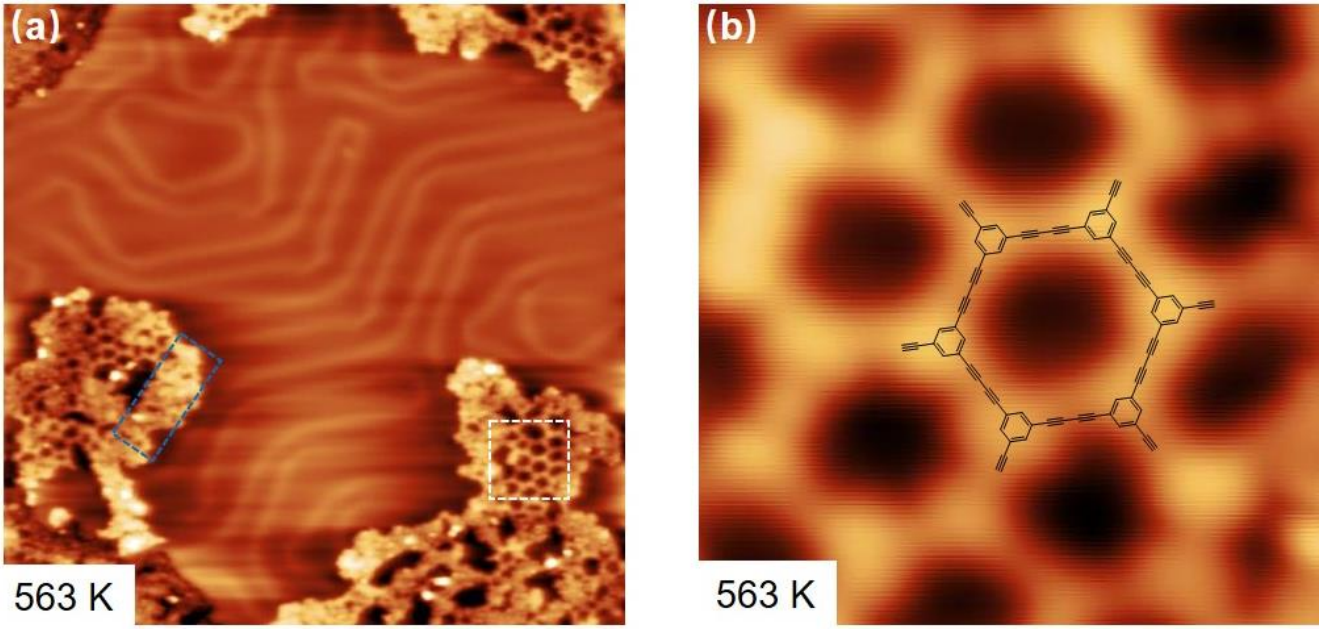


Figure S8. (a) STM image after annealing the sample at 563 K. (b) Zoom-in image of the white dashed frame in (a) shows the covalent networks. Scanning parameters: *U* = -1.0 V, *I* = 0.1 nA.

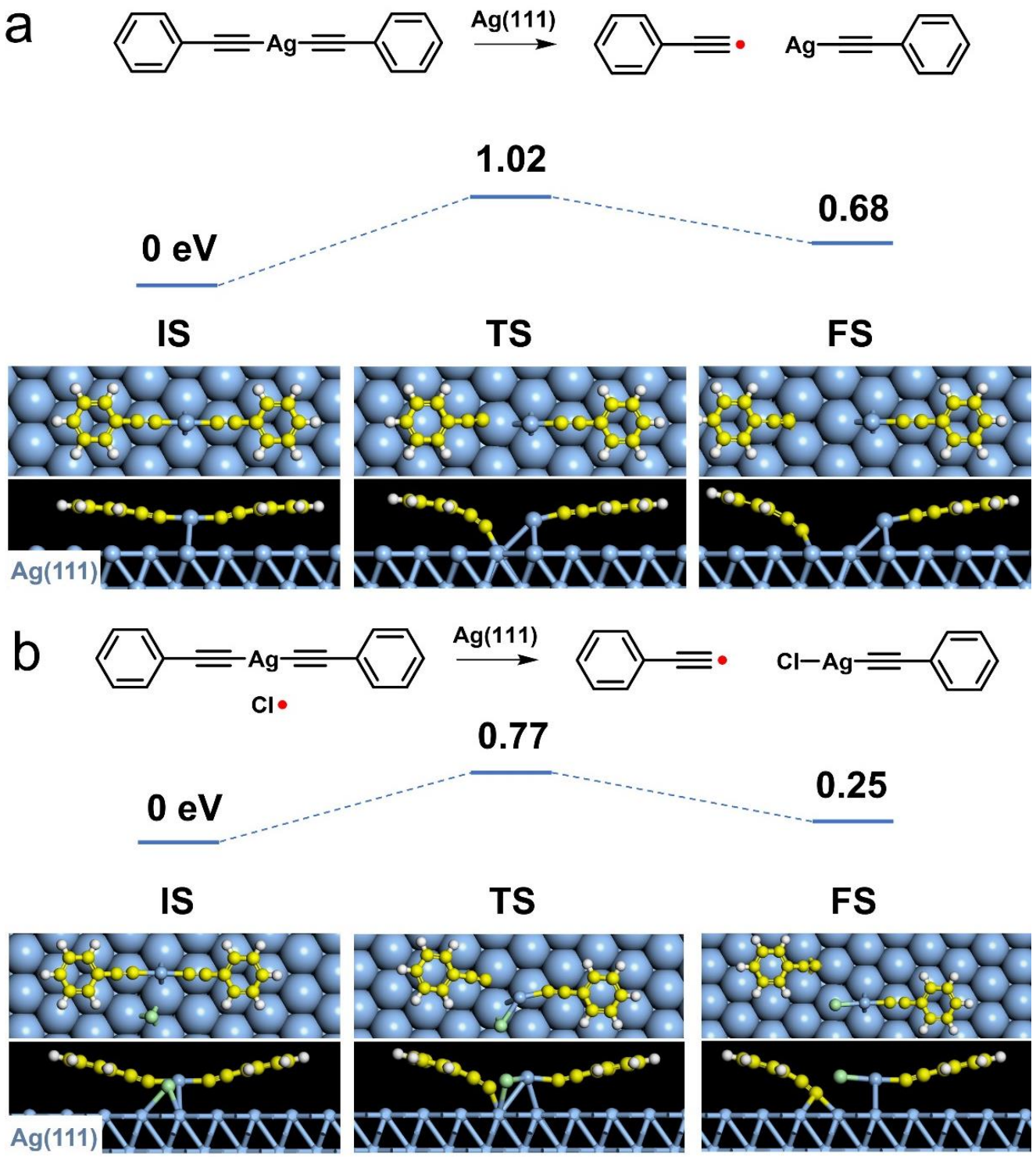


Figure S9. Top and side views of the initial state (IS), transition state (TS), and final state (FS) for the reaction on Ag(111). a) Break of Ag-alkynyl bonds without the assistance of chlorine atom; b) Break of Ag-alkynyl bonds with the assistance of a chlorine atom.

5. References

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(3) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.

(4) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.

(5) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(6) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correctionJ. *Comput. Chem.* **2006**, *27*, 1787.