

Lattice-Directed Selective Synthesis of Acetylenic and Diacetylenic Organometallic Polyynes

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Cu(110). The DFT calculations indicate that such a lattice dependence of skeleton reconstruction originates from the thermodynamic stability of diacetylenic Ag-carbyne/acetylenic Cu-carbyne on the corresponding surfaces.

INTRODUCTION

Carbyne, an infinite chain of sp-hybridized carbon atoms with highly delocalized π -electrons, is envisioned as a good candidate in emerging optical and electronic applications due to its extraordinary nonlinear optical effects and unusual electron transport properties.^{1–3} Herein, the coupling of π -electrons and bond alternations between neighboring carbon atoms is decisive in the physical properties of the carbon chain, namely, a cumulenic form resulting in a conductor and a polyynic form resulting in a semiconductor.^{4,5} On the other hand, the incorporation of transition metals into polymeric carbon scaffolds enables the combination of the transition metals with d electrons and the carbons with π -electrons, which further opens an avenue for tuning their electronic, optical, and magnetic properties.^{6–8} In this regard, organometallic polyynes (i.e., metalated carbynes), belonging to polymetallaynes, are composed of alternating metal atoms and finite carbon atoms (the number of carbon atoms within the chain structures could be 2, 4, 6, etc.). Such metal incorporated polymers were first synthesized with Group 10 metals (Ni, Pd, Pt).9 The organometallic chemistry of Group 11 (Cu, Ag, Au) metalacetylide polymers has also aroused considerable interest because of their fascinating physical and chemical properties, particularly in luminescence and nonlinear optics.^{10–12} In fact, the electronic properties of these organometallic polyyne complexes can be modified by the nature of the transition metals and their coordination as well as the length of acetylenic units.^{13,14} However, these polymers often suffer from a lack of solubility and intrinsic instability, which hampers their preparation and characterization.^{15,16}

In contrast to traditional solution chemistry, on-surface synthesis holds particular potential for the formation of poorly soluble or insoluble polymers owing to its solvent-free reaction environment. As a bottom-up strategy, on-surface synthesis is advantageous for the fabrication of atomically precise nanostructures.^{17–22} Furthermore, the availability of different metal substrates accompanied by varying lattices allows for a delicate control of reaction products.^{23–27} More importantly, with the assistance of high-resolution scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM), the atomic-scale and single-bond-resolved structures could be unambiguously identified. Very recently, by such an on-surface synthesis method, we have achieved the formation of two kinds of organometallic polyynes of Group 11 (i.e., Au- and Cucarbyne), respectively.^{28,29} It is of utmost interest to further expand the organometallic polyyne family, especially with the aim of developing a general strategy to control the incorporated metal elements and the acetylenic units.

Received: November 21, 2021 Revised: January 22, 2022



Scheme 1. Schematic Illustration Showing the Formation of Acetylenic and Diacetylenic Ag- and Cu–carbyne through Dehalogenative Polymerization from the C_2I_4 and C_4Br_4 Precursors^{*a*}



^aNote that the acetylenic Ag-carbyne can be transformed to the diacetylenic one and the diacetylenic Cu-carbyne can be transformed to the acetylenic one by thermally induced skeleton reconstruction.



Figure 1. (a) Schematic illustration showing the formation of the acetylenic Ag–carbyne from C_2I_4 molecules on Ag(110) at 300 K. (b) STM image of the assembled acetylenic Ag–carbyne with a Moiré pattern along the [110] direction of the Ag(110) substrate. (c) Close-up STM image of a single acetylenic Ag–carbyne chain on Ag(110). The detached I atoms are indicated by blue circles. (d) Equally scaled high-resolution nc-AFM image, simultaneously acquired STM image together with STM simulation, and DFT-optimized model of the acetylenic Ag–carbyne chain on Ag(110). The height difference between the topmost and bottommost Ag atoms within the chain is indicated. Scale bars: 4 Å. The unit cell of the model is indicated in Figure S3. Color code: C, gray; organometallic Ag, blue; substrate Ag, cyan (first layer) and brown (underlayer). (e and f) Linescan profiles along the positions marked by A–B and A'–B' in (c). STM scanning parameters: (b) $V_t = -1.8$ V, $I_t = 0.9$ nA; (c) $V_t = -2.0$ V, $I_t = 0.7$ nA.

In this work, to explore the formation of Ag-carbyne, the third type of metalated carbyne in Group 11, we choose a simple molecule (1,1,2,2-tetraiodoethylene, shortened as C_2I_4), which is functionalized with two alkenyl gem-diiodide groups, as shown in Scheme 1. Moreover, the 1,1,4,4-tetrabromo-1,2,3-butatriene molecule (shortened as C_4Br_4) is introduced for the fabrication of organometallic polyynes with diacetylenic units. By combining STM and nc-AFM imaging together with density functional theory (DFT) calculations, we demonstrate that (i) the formation of two kinds of Ag-carbyne (i.e., the acetylenic and diacetylenic Ag-carbyne) is achieved on the Ag(110) surface and (ii) the irreversible transformation of acetylenic Agcarbyne to the diacetylenic counterpart occurs by heating up the sample. Interestingly, on the Cu(110) surface, the diacetylenic Cu-carbyne would irreversibly transform to the acetylenic one by heating up the sample. Our DFT calculations indicate that such a lattice-directed skeleton reconstruction on surfaces originates from the thermodynamic stability of diacetylenic Agcarbyne/acetylenic Cu–carbyne on the corresponding surfaces; (iii) the calculated band structures and the density of states (DOS) of organometallic polyynes reveal that the polyynic moiety derived energy bandgaps decrease with the increasing number of acetylenic units and are metal dependent with the order of Ag–carbyne > Cu–carbyne > Au–carbyne.

EXPERIMENTAL SECTION

Experiments were carried out in two independent ultrahigh vacuum systems that host a SPECS variable-temperature "Aarhus-type" and a low-temperature Omicron scanning tunneling microscope, respectively, where the base pressures were $\sim 1 \times 10^{-10}$ mbar. The STM images were taken in the constant-current mode, and the voltage is applied on the sample. STM imaging parameters: $V_t = -0.3 \sim -1.5$ V, $I_t = 0.7-1.0$ nA. The nc-AFM measurement was carried out at the LHe temperature in constant-height frequency modulation mode with a CO-functionalized tip (resonance frequency of $f_0 = 40.7$ kHz, $Q \approx 5.6 \times 10^4$, oscillation amplitude ≈ 100 pm). The Ag(110) and Cu(110) substrates were prepared by several cycles of 1.5 keV Ar⁺ sputtering



Figure 2. (a) Schematic illustration showing the structural transformation from acetylenic Ag–carbyne to diacetylenic Ag–carbyne after annealing at 470 K. (b) Large-scale and (c) close-up STM images of the diacetylenic Ag–carbyne chain along the [001] direction of the Ag(110) substrate. (d) Linescan profile along the blue dashed line in (c). (e) DFT-optimized model and the corresponding simulated STM image of an individual diacetylenic Ag–carbyne chain on Ag(110). STM scanning parameters: (b) $V_t = -0.3$ V, $I_t = 0.8$ nA; (c) $V_t = -0.2$ V, $I_t = 0.7$ nA.

followed by annealing to 850 K, resulting in clean and flat terraces separated by monatomic steps. After the system was thoroughly degassed, the C_2I_4 (from TCI, purity > 97%) and the C_4Br_4 molecule (synthesized³⁰) were sublimated at 300 K from the molecular evaporator onto the substrate. The sample was thereafter transferred within the UHV chamber to the microscope, where measurements were carried out in a typical temperature range of 100–150 K.

The band structure calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP).^{31,32} The projector-augmented wave method was used to describe the interaction between ions and electrons,^{33,34} and the Perdew–Burke– Ernzerhof generalized gradient approximation exchange-correlation functional was employed.³⁵ van der Waals corrections to the PBE density functional were also included using the DFT-D3 method of Grimme.³⁶ Both of the Ag(110) and Cu(110) surfaces were modeled as a three-layer slab vertically separated by a vacuum region of 15 Å. The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms, except the bottom layers of the corresponding slab (keep fixed), were $\leq 0.03 \text{ eV/Å}$. The simulated STM images were obtained by the Hive program based on the Tersoff-Hamann method.37 The band structures and projected DOS were calculated with the Quantum Espresso software package³⁸ using the PBE exchange-correlation functional.³⁵

The spin polarized band structure calculations were performed for the acetylenic, diacetylenic, and triacetylenic Ag–carbynes by using the Vienna ab initio simulation package (VASP).^{31,32} In order to obtain high-precision band structure, the hybrid functional (HSE06)³⁹ was employed. The cutoff energies were set to be 500 eV. The K point was set to be $1 \times 1 \times 7$ in the geometry optimization. The K point was increased to $1 \times 1 \times 19$ for the further SCF calculation. For the band structure calculation, the K point was set along the atomic chains. The



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Figure 3. (a) Schematic illustration showing the direct formation of the diacetylenic Ag–carbyne structures after deposition of C_4Br_4 molecules on Ag(110) held at 300 K. (b) Large-scale and (c) close-up STM images of the diacetylenic Ag–carbyne chain on Ag(110). The detached Br atoms are indicated by blue circles. (d) Linescan profile along the blue dashed line in (c). STM scanning parameters: (b) $V_t = 1.8$ V, $I_t = 0.9$ nA; (c) $V_t = 1.3$ V, $I_t = 1.0$ nA.

vacuum space was set to be 12 Å to avoid the interactions between periodical images.

RESULTS AND DISCUSSION

After deposition of C_2I_4 molecules on Ag(110) held at room temperature (RT), we observe the formation of ribbon structures along the [110] direction of the substrate, which are composed of individual molecular chains with a clear Moiré-like pattern as shown in Figure 1b. Such a chain structure resembles our previously reported Au-incorporated organometallic polyyne formed by dehalogenative polymerization of C_4Br_4 molecules on the Au(111) surface.²⁹ Likewise, we naturally assign the formed chain structures (Figure 1b) to Agincorporated organometallic polyynes (i.e., Ag-carbyne), which is illustrated in the upper panel of Scheme 1 and Figure 1a. The close-up STM image of a single Ag-carbyne chain is shown in Figure 1c. The single Ag-carbyne chain is rare on the surface, and the ratio of the assembled and single chains is about 9:1 as shown in Figure S1. From the comparison of the nc-AFM image, STM image, STM simulation, and DFT model of the Ag-carbyne chain (Figure 1d), the characteristic protrusions corresponding to C-C triple bonds are resolved by nc-AFM imaging as in the case of Cu-carbyne and Au-carbyne.^{28,29} The bright protrusions within the chain are in relation to the high electronic density of states of Ag atoms from STM imaging. We therefore identify that the formed Ag-carbyne should be assigned to acetylenic Ag-carbyne. It is noted that Ag atoms within the chain have different adsorption heights, and the height difference between the highest and lowest Ag atoms is



Figure 4. (a) Schematic illustration showing the formation of diacetylenic and acetylenic Cu–carbyne on Cu(110). (b) Large-scale and (c) close-up STM images showing the formation of diacetylenic Cu–carbyne chains along the [001] direction after deposition of C₄Br₄ molecules on Cu(110) held at 300 K. The detached Br atoms are indicated by blue circles in (c). (d) DFT-optimized model of a single diacetylenic Cu–carbyne on Cu(110) and linescan profile along the blue dashed line in (c). (e) Large-scale and (f) close-up STM images showing the formation of acetylenic Cu–carbyne chains along the [110] direction after annealing at 450 K. (g) DFT-optimized model of a single acetylenic Cu–carbyne on Cu(110) (color code: C, gray; organometallic Cu, wine; substrate Cu, pink (first layer), brown (underlayer)) and linescan profile along the blue dashed line in (f). STM scanning parameters: (b and c) $V_t = -1.5$ V, $I_t = 1$ nA; (e and f) $V_t = -1.7$ V, $I_t = 0.5$ nA.

0.24 Å determined by DFT calculations. This results in a 1D Moiré superlattice and presents a super periodicity in the STM images (shown in both assembled and single acetylenic Agcarbyne). Such a Moiré lattice is attributed to the incommensurate registry between the acetylenic Ag-carbyne and the underlying substrate lattice along the $[1\overline{10}]$ direction. As shown in the A–B linescan profile (Figure 1c,e), the super periodicity of the Moiré pattern is measured to be 37.4 ± 1.0 Å, and the distance between Ag atoms within acetylenic Ag-carbyne is 5.4 \pm 0.2 Å. These experimental results are also in good agreement with the DFT calculations. For comparison, the A'-B' linescan profile (Figure 1f) performed over a bare surface region presents a periodicity of 3.0 Å \pm 0.2 Å, which corresponds to the Ag(110) lattice spacing along the [110] direction (cf. 2.89 Å). In comparison with the formation of isolated Cu-carbyne chains,²⁸ formation of assembled Ag-carbyne is attributed to the presence of halogen atoms that can intercalate beneath the molecular structures, 40,41 thus facilitating the movement of Ag– carbyne chains on the surface. A control experiment has been performed as shown in Figure S2 (see details in the Supporting Information).

Due to the incommensurate registry between the acetylenic Ag–carbyne and the underlying lattice, it is interesting to observe that after annealing at 470 K the organometallic polyyne chains turn to the [001] direction of the Ag(110) substrate (Figure 2b). In addition, the periodicity of the chain structure becomes 8.1 ± 0.2 Å (Figure 2c,d), which coincides with twice the length of the lattice spacing along the [001] direction of Ag(110) (cf. 8.18 Å), resembling the previously reported case of

diacetylenic Au–carbyne.²⁹ We then naturally assign the formed chain structures to diacetylenic Ag–carbyne (also see Figure 2a). From the DFT calculations shown in Figure 2e, it is seen that the diacetylenic Ag–carbyne has a good match with the underlying substrate lattice, and accordingly, the Moiré pattern also disappears experimentally.

To further confirm the structural transformation from the acetylenic to the diacetylenic Ag-carbyne, we deposit C4Br4 molecules on Ag(110) held at 300 K. It is observed that the dehalogenative polymerization has already occurred on Ag(110)at RT as on Au(111),²⁹ and as a result, we have directly fabricated the diacetylenic Ag-carbyne chains growing along the [001] direction of the substrate, as displayed in Figure 3a,b. The periodicity of the chain is measured to be 7.8 \pm 0.2 Å (Figure 3c,d). In comparison of the morphology and the periodicity, a good agreement is achieved between the thermally induced diacetylenic Ag-carbyne (Figure 2c) and the directly formed one (Figure 3c). Importantly, the diacetylenic Agcarbyne structure remains stable after annealing at 470 K as shown in Figure S4, which indicates that such a diacetylenic Agcarbyne is thermodynamically more stable than the acetylenic one on Ag(110).

We have previously demonstrated that the acetylenic Cu– carbyne could be formed from ethyne molecules on Cu(110),²⁸ and there is no structural transformation that occurred for acetylenic Cu–carbyne at higher temperatures (also see Figure S2). To expand the family of diacetylenic organometallic polyynes, we deposit C₄Br₄ molecules on Cu(110) held at 300 K. As expected, the dehalogenative polymerization has also



Figure 5. DFT calculated band structures and the corresponding DOS of free-standing planar acetylenic, diacetylenic, and triacetylenic (a) Ag–carbyne, (b) Cu–carbyne, and (c) Au–carbyne. The colored areas in yellow are the projections of the DOS from the metals onto the systems. The electronic gaps arising from the carbons are indicated by black dashed lines with arrows together with the gap values in units of electronvolts. The energies are aligned with respect to the vacuum level. The Fermi levels of the systems are indicated by gray dashed lines. Gamma point to the Brillouin zone boundary.

occurred on Cu(110) at RT resulting in the direct formation of diacetylenic Cu–carbyne chains growing along the [001]

direction of the substrate, as displayed in Figure 4a,b. The periodicity of the diacetylenic Cu–carbyne is measured to be 7.4 \pm 0.2 Å (Figure 4c,d).

Interestingly, after annealing at 450 K the organometallic polypne chains turn to the [110] direction of the Cu(110) substrate (Figure 4e), and the periodicity of the chain becomes 5.5 ± 0.2 Å (Figure 4f,g). From the morphology and the dimension of the chain, we identify that the diacetylenic Cu–carbyne has transformed to the acetylenic one (also see Figure 4a), indicating the acetylenic Cu–carbyne is thermodynamically more stable than the diacetylenic one.

In order to understand this lattice-directed transformation between acetylenic and diacetylenic organometallic polyyne chains, we carried out DFT calculations to gain quantitative information for the acetylenic and diacetylenic Ag/Cu–carbyne structures on surfaces, respectively, as shown in Figure S5. It turns out that the diacetylenic Ag–carbyne is calculated to be 4.73 eV more stable than the acetylenic one on Ag(110) (Figure S5a), while on Cu(110) the acetylenic Cu–carbyne is calculated to be more stable than the diacetylenic one by 1.07 eV (Figure S5b). A good agreement is achieved between the experimental observations and the DFT calculations. We thus draw the conclusion that such a lattice-dependent acetylenic skeleton reconstruction originates from the thermodynamic stability of the organometallic polyyne chains on the corresponding surfaces.

A step further, we expand the system of organometallic polyyne chains with triacetylenic moieties by DFT calculations, in which both the band structures and DOS have been systematically calculated as shown in Figure 5. To our knowledge, the electronic properties of the organometallic polyynes crucially depend on the acetylenic skeletons and the nature of incorporated metal elements.^{13,14} Herein, acetylenic, diacetylenic, and triacetylenic Ag/Cu/Au-carbyne chains have been calculated. Wide gap regions are all observed for the calculated organometallic polyynes, which can be attributed to the acetylenic segments as determined from the projected DOS (areas in gray). The energy gaps decrease with the increasing lengths of carbon skeletons from acetylenic over diacetylenic to triacetylenic organometallic polyynes, which is consistent with previous studies.^{13,14,42} Also, it is noted that, for the same carbon skeletons, Au-carbyne has the smallest energy gaps in comparison with Ag- and Cu-carbynes.

More interestingly, the involvement of transition metals in the carbon chain may lead to exotic electronic properties. We then



Figure 6. Spin-polarized band structures (left panels) and the density of states (in the right panels) for the acetylenic, diacetylenic, and triacetylenic Ag–carbynes with their chemical structures displayed on the top. Here, the solid and dotted lines represent the spin up and spin down contributions, respectively. The colors of the bands reflect the weights of the carbon and metal in the bands, i.e., from blue to red means carbon dominated contribution.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the National Natural Science Foundation of China (22125203, 21790351, 21790353, 21972032, 21721002, 21425310, 22072086), the Fundamental Research Funds for the Central Universities, the Ministry of Science and Technology of China (2017YFA0205000 and 2016YFA0200700), and the Strategic Priority Research Program of Chinese Academy of Sciences (XDB36000000). The authors thank Prof. Nancy S. Goroff for supporting the organic synthesis of the C₄Br₄ molecule. Q.S. is grateful for the help from Carlo Pignedoli for band structure calculations.

performed spin-polarized DFT calculations on different Agcarbyne chains to investigate their magnetic properties. The spin-polarized band structures and corresponding DOS of the acetylenic, diacetylenic, and triacetylenic Ag-carbyne chains are shown in Figure 6. Intriguingly, although Ag is not magnetically active, all three organometallic polyynes are spin polarized and exhibit magnetism. Notably, both acetylenic and diacetylenic Ag-carbyne are half-metallic with one of the spin channels crossing the Fermi level while the others are gapped. The net magnetic moments for Ag-carbyne containing acetylenic, diacetylenic, and triacetylenic moieties in each unit cell are determined to be 0.608 $\mu_{\rm B}$, 0.586 $\mu_{\rm B}$, and 0.574 $\mu_{\rm B}$, respectively. To understand the origin of the magnetism, we evaluated the contributions of each atom by projecting the wave functions of the atomic orbitals to the wave functions of the Ag-carbyne chains. The weights of the contributions from carbon and metal are reflected by the blue-red color scale of the bands in Figure 6. We found that the spin-polarized bands are more blue-colored and less reddish, indicating the magnetism is mainly attributed to the carbon contributions rather than Ag. Our findings may lead to a new class of carbon-based magnetic materials, which have been under intensive study recently.^{43–45}

CONCLUSIONS

In conclusion, from a combination of high-resolution STM, nc-AFM imaging, and DFT calculations, we have achieved the selective synthesis of thermodynamically more stable acetylenic or diacetylenic organometallic polyynes on the corresponding Ag(110) and Cu(110) surfaces, respectively, which indicates the important role of the substrate lattice in directing the synthesis of 1D carbon nanostructures. Such 1D organometallic polyynes with theoretically predicted tunable energy bandgaps would shed light on the next generation of semiconducting materials and molecular electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c04015.

Large-scale STM image of the acetylenic Ag–carbyne chains on Ag(110); investigation of the reason for the formation of assembled metalated carbyne structures on the surface; the unit cell of the DFT calculated model of the acetylenic Ag–carbyne on the Ag(110) surface; STM image of the diacetylenic Ag–carbyne chains after annealing at 470 K; and DFT-optimized geometries of the acetylenic and diacetylenic Ag/Cu–carbyne structures on surfaces (PDF)

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