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

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ABSTRACT: One of the most appealing topics in the study of metal–organic networks is the growth mechanism. However, its study is still considered a significant challenge. Herein, using scanning tunneling microscopy, the growth mechanisms of metal–alkynyl networks on Ag(111) and Au(111) surfaces were investigated at the atomic scale. During the reaction of 1,3,5-tris(chloroethyl)benzene on Ag(111), honeycomb Ag-alkynyl networks formed at 393 K, and only short chain intermediates were observed. By contrast, the same precursor formed honeycomb Au–alkynyl networks on Au(111) at 503 K. Progression annealing led to a stepwise evolution process, in which the sequential activation of three Cl-alkynyl bonds led to the formation of dimers, zigzag chains, and novel chiral networks as the intermediates. Moreover, density functional theory calculations indicate that chlorine atoms are crucial in assisting the breakage of metal-alkynyl bonds to form Cl-metal-alkynyl, which guarantees the reversibility of the break/formation equilibration as the key to forming regular large-scale organometallic networks.

INTRODUCTION

Metal–organic networks (MONs) have attracted significant attention recently as part of the emerging field of two-dimensional (2D) materials.1 Furthermore, remarkable progress has been made in the design and preparation of MONs, with superb structural, chemical, and functional tunability.2 One of the vital aspects in achieving novel structures and prominent properties for MONs is the in-depth understanding of their growth mechanism, which has thus far remained a significant challenge.3 Taking advantage of the atomic resolution of scanning tunneling microscopy (STM),3 MONs constructed on well-defined surfaces can be directly visualized,3 which provides the opportunity to investigate their growth mechanism at the atomic scale. For example, the hierarchical assembly of 1,3,5-tricarboxylic benzoic acid and Fe atoms was reported on Cu(100), and successive aufbau structures with increasing complexities were observed after progression annealing.4 Later, distinct MONs were reported using varying ratios of europium and linkers, including 4-, 5-, and 6-fold vertices.5a We also reported a multistep non-reversible structural transformation of MONs by increasing the surface molecular density.6 However, because the MON formation process is highly complex and dynamic,6 acquiring an in-depth understanding of the stepwise growth mechanism of MONs is a significant challenge.

Owing to the π−π overlap between metals and alkynyl groups, the metal–alkynyl moiety demonstrates a strengthened metal–carbon bond and an extended π-electron delocalization.9 Thus, organometallic structures containing metal–alkynyl moieties exhibit intriguing conductive, magnetic, and optical properties.10 The on-surface preparation of organo-metallic honeycomb networks comprising Au–alkynyl units has been previously reported from a precursor of 3-fold symmetry containing Br-alkynyl through annealing on Au(111) at 320 K.11 Similarly, the formation of honeycomb Ag–alkynyl networks has been achieved through the activation of Br–alkynyl bonds on Ag(111) at room temperature.12 Interestingly, honeycomb Ag–alkynyl networks can also be prepared through an oxygen-mediated surface reaction of H-alkynyl bonds in 1,3,5-tris(4-ethynylphenyl)benzene.13 Recently, Wu and co-workers reported a dissymmetric reaction of a bifunctional precursor with H-alkynyl and Br-phenyl substituents for the construction of binodal organometallic networks, which contain both alkynyl–Ag–alkynyl and alkynyl–Ag–phenyl nodes.14

Because the organometallic bond strength of Ag(Au)–alkynyl is stronger than those of the coordination bonds such as M–N or M–O,15 we assume that the intermediates formed during the organometallic network formation process may be more stable and easier to identify. Moreover, the formation of regular organometallic networks comprising Ag(Au)–alkynyl constituents requires higher temperatures, which may offer an opportunity to monitor the growth mechanism using a temperature progression approach.
Because of the higher bond strength and resulting lower reactivity of the C–Cl bond in comparison with those of the C–Br bond, we observed a sequential and stepwise activation of the C–Cl bond during the coupling process of Scheme 1.
the CCl$_3$ group. Thus, in this study, we designed 1,3,5-tris(chloroethynyl)benezene (tCEB) (Scheme 1) as the precursor and investigated the assembly pathways during the formation of honeycomb Ag(Au)–alkynyl networks on Ag(111) and Au(111) surfaces. Remarkably, these pathways were different for Ag(111) and Au(111). Distinct transient products and regular network phases were observed on Au(111), including chiral motifs and network types. The experimental observations and density functional theory (DFT) calculations suggested that chlorine atoms play important roles in surface chemical conversions and are a decisive factor for forming regular metal–alkynyl networks.

Results and Discussion

Growth Mechanism of Honeycomb Ag–Alkynyl Networks on Ag(111). The deposition of tCEB onto the surface of Ag(111) at 150 K resulted in the formation of disordered short chain structures (Figure 1a). Figure 1b shows a magnified STM image, in which a chemical structure is fitted on it. Detached chlorine atoms (marked with the green dashed circle) were observed to assemble along the alkynyl networks (unit cell of $a = b = 21.3 \pm 0.8 $ Å, $\theta = 120^{\circ}$), which match well with the chemical structure fitted on it. Detached chlorine atoms (marked with the green dashed circle) were observed to assemble along the honeycomb networks. The distance between the benzene rim and the center of the chlorine atom was measured to be $2.7 \pm 0.2$ Å, which agrees with the DFT-calculated distance (see Figures S2 and S3). Moreover, the atoms-in-molecules (AIM) analysis suggested that the bond energy of the Cl···H interaction was $-71.1$ meV, which confirmed the stabilization effect of the chlorine atoms on the honeycomb networks (see Figure S3). The efficient transformation from irregular structures to honeycomb Ag–alkynyl networks at a mild annealing temperature of $393$ K demonstrated a good reversibility of the break/formation reactions of the Ag–alkynyl bond on the Ag(111) surface. This facilitated the self-healing process for repairing irregular rings that were observed in the irregular organometallic networks to afford thermodynamically stable honeycomb networks.

Growth Mechanism of Honeycomb Au–Alkynyl Networks on Au(111). The formation of honeycomb Au–alkynyl networks on the surface of Au(111) may require a higher annealing temperature owing to the lower reactivity of gold compared to that of silver. Thus, the potential intermediates may be more stable and easier to monitor with...
the temperature progression approach. Next, we discuss the on-surface synthesis of large-scale honeycomb Au−alkynyl networks, which is achieved by the thermal treatment of tCEB on the less reactive surface of Au(111).

We deposited a submonolayer of tCEB on Au(111) at 150 K, which resulted in the formation of two phases. A close packing of tCEB monomers and dimers is shown in Figure 2a, in which unreacted tCEB molecules can be found (as indicated by the white dashed circle). As shown in image (1) of Figure 2b, the length from the benzene center to the Cl end was measured as 5.6 ± 0.2 Å, which was consistent with the distance obtained by the DFT calculations (5.7 Å). It is worth noting that the unreacted tCEB had a low concentration of less than 5%, suggesting that the Cl−alkynyl bond can also be efficiently activated on the Au(111) surface at 150 K. Image (2) of Figure 2b shows a tCEB in which one Cl−alkynyl is activated to form Cl−Au-alkynyl. The Cl−Au−alkynyl moiety is evidently different from Cl−alkynyl; this is because the Au atom appears as a bright round protrusion, whereas the adjacent C≡C group becomes dim.11,19 The distance between the benzene center and the Cl end in the reacted tCEB was measured as 8.4 ± 0.2 Å, which was consistent with the distance obtained through the DFT calculations (8.3 Å). Figure 2c shows another phase observed in the same sample at 150 K, which consists of self-assembled dimers of tCEB. The magnified image in Figure 2d shows that the alkynyl groups of two tCEB units in a dimer are linked by a gold atom. The length between the two benzene rings obtained by STM measurement was 12 ± 0.5 Å; this value was consistent with that obtained through the DFT calculations (12.0 Å).

When the sample was annealed at 300 K, the resulting structures were composed of 46% dimers and 54% short zigzag chains (Figure 2e). The magnified image in Figure 2f shows short zigzag chains fitted with chemical structures. Subsequently, the activation of the second Cl−alkynyl bond occurred, which linked the tCEB units into zigzag chains. As indicated by the white dashed circle, two Cl−Au−alkynyl substitutes assemble in the vicinity position, thereby suggesting that a further reaction might occur between the two Cl−Au−alkynyl substitutes to form a longer zigzag chain. It is worth noting that the deposition of tCEB on the Au(111) surface at 150 K had no obvious impact on the Au(111) herringbone reconstruction. However, after annealing the sample at 300 K, the Au(111) herringbone reconstruction was altered, as shown in Figure S4. This phenomenon may be attributed to the activation of Cl−alkynyl, which may lift the Au atoms from the Au(111) herringbone reconstruction.20 When the sample was annealed to 393 K, the tCEB units were linked to form significantly longer zigzag chains, which self-assembled in a staggered arrangement to form a compact structure, as shown.

Figure 3. Growth process forming honeycomb Au-alkynyl networks on Au(111). (a, b) Large-scale and magnified STM images on Au(111) annealed at 423 K. (c, d) Large-scale and magnified STM images of chiral Au-alkynyl networks on Au(111) annealed at 453 K. (e, f) Large-scale and magnified STM images of honeycomb Au−alkynyl networks on Au(111) annealed at 503 K. (i) Proposed formation mechanism of chiral Au−alkynyl networks. The detached chlorine atoms were marked with green dashed circles. Scanning parameters (a−i): $U = -1.0$ V, $I = 0.1$ nA.
in Figure 2g. The structural fitting in the magnified image (Figure 2h) illustrates that the zigzag chains are Au−alkynyl complexes, in which two Cl−alkynyl bonds are activated and only one Cl−alkynyl bond remains intact.

When the sample was annealed at 423 K, a part of the ordered self-assembled zigzag chains broke down to form a mixture of hexagons and chain structures (Figure 3a). As shown in the magnified image in Figure 3b, a hexagonal structure is composed of six tCEB units and six Au atoms as linkers. It is worth noting that Cl−alkynyl (white dashed circle) and Cl−Au−alkynyl (red dashed circle) substituents coexisted at this annealing temperature.

Upon annealing the sample at 453 K, the activation of three Cl−alkynyl bonds was completed, and the hexagons were unexpectedly connected to form novel chiral Au−alkynyl networks with a unit cell of \( a = b = 42.0 \pm 0.8 \text{ Å}, \theta = 120^\circ \) (Figure 3c,d). As shown in Figure 3d, this interesting arrangement can be regarded as a regular hexagon core with six circumambient-distorted hexagons. Note that two enantiomeric networks, which have been indicated as clockwise (CW) and counterclockwise (CCW), coexist in the sample (Figure 3c). A careful inspection of the chiral Au−alkynyl networks reveals that every set of three regular hexagons is linked by a tCEB unit that has been rotated at an angle of 28° (Figure 3d). In the sample annealed at 423 K, single hexagons are prevalent, whereas a single molecule with three Cl−Au−alkynyl substituents (see the inset in image 2 of Figure 3i) can also be found. Therefore, as depicted in Figure 3i, we propose that the formation of the chiral Au−alkynyl networks may proceed through the following processes: the assembly of three hexagons and a tCEB linker (image 2), the subsequent rotation of the tCEB linker (image 3), and its reaction with three hexagons (image 4). The DFT calculations of the structures shown in images 3 and 4 indicate that the Au and benzene rings are located in the stable bridge and hollow sites of the Au(111) surface, respectively. Afterward, the resulting structure (image 5) may propagate to afford chiral Au−alkynyl networks (image 6).

It is worth noting that the honeycomb Au−alkynyl networks could also be found in the gap between the blue and white dashed lines (Figure 3e), thereby suggesting that the chiral networks might be fragmented and then transform into the honeycomb networks. The magnified image in Figure 3f shows detailed structures of the fragments and the newly formed honeycomb Au−alkynyl networks. A statistical analysis of the STM data showed that the ratio of the chiral Au−alkynyl networks to the honeycomb Au−alkynyl networks increased to 9:7 at 473 K. To clarify the driving force responsible for the transformation of the chiral networks to the honeycomb networks, we conducted DFT calculations to compare the energies of the nonlinear alkynyl−Au−alkynyl moiety with a distortion angle of 28° and the linear alkynyl−Au−alkynyl moiety (Figure S5 in the SI). The results demonstrated that the linear moiety was more stable than the nonlinear moiety, and that the stabilization energy was 0.18 eV.

When the sample was further annealed to 503 K, the chiral Au−alkynyl networks disappeared and the more stable honeycomb Au−alkynyl networks were dominant on the surface as the thermodynamic product (Figure 3g). Note that the honeycomb Au−alkynyl networks formed on the Au(111) surface represent multiple domains (20−55 nm², Figure S6), which is in contrast to the single domain of honeycomb Ag−alkynyl networks formed on the Ag(111) surface. This can be attributed to the higher stability of the Au−alkynyl bond formed on the Au(111) surface, which leads to a relatively poor reversibility of the break/formation equilibration. The magnified STM image presented in Figure 3h shows the detailed structure of the honeycomb Au−alkynyl networks with a unit cell of \( a = b = 21.3 \pm 0.8 \text{ Å}, \theta = 120^\circ \), which is in agreement with that obtained in a previous study. Similar to the case of honeycomb Ag−alkynyl networks, the detached chlorine atoms were observed to assemble along the intermediate structures and honeycomb networks on Au (111). The stabilization effect of chlorine atoms on the structures was revealed through AIM analysis. The Cl···H interactions were detected, and their bond energies varied from −5.70 to −90.1 meV (Figure S7).

We also tried a higher annealing temperature to convert honeycomb Au−alkynyl networks into covalent networks. After annealing at 563 K, the desorption of chlorine atoms occurred, and the organometallic networks converted into complicated and irregular structures in which only small...
patches of covalent networks could be observed (see Figure S8). Thus, high-temperature annealing is not a good way to convert current organometallic networks into 2D covalent networks.

**DFT Calculations for the Breakage of Metal–Alkynyl Bonds.** The reversibility of the break/formation of metal–alkynyl bonds plays a key role in the formation of thermodynamic products on metal surfaces. Therefore, DFT calculations were conducted on the Au(111) and Ag(111) surfaces to evaluate the breaking of the metal–alkynyl bond using a simplified molecular model, (chloroethynyl)benzene (CEB). The reaction barrier and reaction energy required to break the Ag–alkynyl bond on the Ag(111) surface were calculated as 1.02 and 0.68 eV, respectively (Figure 4a, blue line). By contrast, breaking the Au–alkynyl bond on the Au(111) surface requires a high barrier energy of 1.43 eV, and the reaction is highly endothermic with a large energy consumption of 1.24 eV (Figure 4a, brown line). The high reaction barrier suggests that breaking the Au–alkynyl bond on Au(111) would be rather difficult. However, this is contradictory to the experimental fact that the reversibility of the break/formation of the Au–alkynyl bond is rather good for forming large-scale chiral and honeycomb Au–alkynyl networks at 453 and 503 K, respectively.

Numerous detached chlorine atoms were observed to assemble alongside the Au-alkynyl bond during the experiments, and the complexes incorporating Cl–Au–alkynyl were frequently detected during the growth process on the Au(111) surface. Therefore, we suspected that the chlorine atoms may assist the breaking of the Au-alkynyl bond by forming Cl–Au–alkynyl complexes. We conducted DFT calculations according to this assumption. The barrier and reaction energy decreased to 0.90 and 0.25 eV, respectively, for the breaking of the Au–alkynyl bond (Figure 4b, brown line). These results are in accordance with our experimental findings. Furthermore, the reaction barrier and reaction energy required to break the Ag–alkynyl bond with the assistance of chlorine atoms were also reduced to 0.77 and 0.25 eV (Figure 4b, blue line), respectively. This result is also in good agreement with the experimental findings of the fast process forming honeycomb Ag-alkynyl networks on Ag(111).

**CONCLUSIONS**

In summary, the stepwise growth mechanism of organometallic metal–alkynyl networks, utilizing the tCEB precursor with a 3-fold symmetry, was visualized at the atomic scale by progression annealing. On Ag(111), the honeycomb Ag–alkynyl networks formed at 393 K and only short-chain intermediates were observed during the formation process. On Au(111), honeycomb Au–alkynyl networks were formed at 503 K, and the sequential activation of three Cl-alkynyl bonds led to the generation of intermediates such as dimers, zigzag chains, and novel chiral Au–alkynyl networks. By combining the experimental observations and DFT calculations, the formation mechanism of the novel chiral Au–alkynyl networks is elucidated along with the driving force that forms honeycomb Au–alkynyl networks. In addition, the DFT calculations indicate that chlorine atoms assist the breakage of metal–alkynyl bonds, reduce the reaction barrier, and stabilize the networks on Au(111) and Ag(111). These results are coherent with the large-scale growth of regular metal–alkynyl networks and the stepwise formation process on Au(111). Furthermore, our findings provide important new insights into the growth mechanism and dynamics of organometallic networks, which may lead to novel approaches to realize high-quality 2D networks with superb structural, chemical, and functional tunability.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c04311.

Detailed descriptions of experimental and theoretical procedures, and additional STM and DFT calculation results (PDF)

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**Notes**

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ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21421004, 21925201, 91845110, and 21672059), Shanghai Municipal Science and Technology Major Project (Grant No. 2018SHZDZX03), the Program of Introducing Talents of Discipline to Universities (B16017), Program of the Shanghai Committee of Sci. & Tech. (Project No. 18520760700), and the Program for Eastern Scholar Distinguished Professor. We thank Dr. Shao-Ze Zhang in Kunming University of Science and Technology for his help in AIM analysis. We thank the Research Center of Analysis and Test of East China University of Science and Technology for help in the characterization.

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