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

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KEYWORDS: Organometallic networks, Surfaces, Growth mechanism, Scanning tunneling microscopy, Density functional theory calculations

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(chloroethynyl)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 twodimensional (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),⁴ MONs constructed on well-defined surfaces can be directly visualized,⁵ 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.⁶ Later, distinct MONs were reported using varying ratios of europium and linkers, including four-, five-, and six-fold vertices.^{5a} We also reported a multi-step nonreversible structural transformation of MONs by increasing the surface molecular density.7 However, because the MON formation process is highly complex and dynamic,8 acquiring an in-depth understanding of the stepwise growth mechanism of MONs is a significant challenge.

Owing to the $p\pi$ -d π overlap between metals and alkynyl groups, 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 organometallic honeycomb networks comprising Au-alkynyl units has been previously reported from a precursor of threefold 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 coworkers 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,¹² 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,¹⁵ we observed a sequential and stepwise activation of the C-Cl bond during the coupling process of the CCl₃ group.¹⁶ 1,3,5-Thus, in this study. we designed tris(chloroethynyl)benzene (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

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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 metalalkynyl 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 (Fig. 1a). Fig. 1b shows a magnified STM image, in which a chemical structure is fitted and the protrusions in the chains are attributed to the Ag atoms.^{12,17} The measured length $(12 \pm 0.5 \text{ Å})$ between the two benzene rings agrees with the DFT-calculated length (12.1 Å). Therefore, in the chain structure, two Cl-alkynyl bonds are activated, and one Clalkynyl bond remains intact in the tCEB unit.

When the sample was annealed at 300 K, irregular organometallic networks formed, as shown in Fig. 1c. A magnified image (Fig. 1d) shows a network in which all three Cl-alkynyl bonds of tCEB are activated, and the structural fitting corroborates the STM results. A large-scale statistical analysis indicated that 74% of the networks were hexagonal, whereas the other 26% were irregular (four-, five-, and seven-membered) rings, thereby suggesting the occurrence of kinetic trapping during the formation of Ag-alkynyl networks at room temperature.¹⁸ The results indicate that the formation of organometallic networks on Ag(111) is a fast process, in which the stepwise growth mechanism is difficult to monitor when using the temperature progression approach.

By increasing the annealing temperature to 393 K, the irregular organometallic network transformed to a single domain of large-scale honeycomb Ag-alkynyl networks (Fig. 1e and Fig. S1 in the Supporting Information). The magnified image in Fig. 1f shows the detailed structures of the honeycomb Ag-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 honevcomb networks. The distance between the benzene rim and the center of the chlorine atom was measured to be 2.7 ± 0.2 Å, which agrees with the DFT-calculated distance (see Fig. 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 Fig. S3). The efficient transformation from irregular structures to honeycomb Agalkynyl 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.

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Figure 1. Growth process of tCEB forming honeycomb Ag-alkynyl networks on Ag(111). (a, b) Large-scale and magnified STM images of tCEB deposited on Ag(111) at 150 K. (c, d) Large-scale and magnified STM images of irregular Ag-alkynyl networks on Ag(111) annealed at 300 K. (e, f) Large-scale and magnified STM images of honeycomb Ag-alkynyl networks on Ag(111) annealed at 393 K. The detached chlorine atoms are marked by the green dashed circles. Scanning parameters (a-f): U = -1.0 V, I = 0.1 nA.

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.^{18b} 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 largescale honeycomb Au-alkynyl networks, which is achieved by the thermal treatment of tCEB on the less reactive surface of Au(111).

We deposited a sub-monolayer 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 Fig. 2a, in which unreacted tCEB molecules can be found (as indicated by the white dashed circle). As shown in image (1) of Fig. 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 Fig. 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 $C \equiv C$ 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). Fig. 2c shows another phase observed in the same sample at 150 K, which consists of self-assembled

dimers of tCEB. The magnified image in Fig. 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 (Fig. 2e). The magnified image in Fig. 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 Fig. 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 in Fig. 2g. The structural fitting in the magnified image (Fig. 2h) illustrates that the zigzag chains are Au-alkynyl complexes, in which two Clalkynyl bonds are activated and only one Cl-alkynyl bond remains intact.



Figure 2. Growth process of tCEB on Au(111) surface. (a, b) Large-scale and magnified STM images containing tCEB monomers on Au(111) at 150 K. (c, d) Large-scale and magnified STM images of dimers on Au(111) at 150 K. (e, f) Large-scale and magnified STM images of short zigzag chains on Au(111) annealed at 300 K. (g, h) Large-scale and magnified STM images of long zigzag chains on Au(111) annealed at 393 K. The detached chlorine atoms were marked with the green dashed circles. Scanning parameters (a), (c-h): U = -1.0 V, I = 0.1 nA; b, U = -0.5 V, I = 0.1 nA.

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 (Fig. 3a). As shown in the magnified image in Fig. 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 $a = b = 42.0 \pm 0.8$ Å, $\theta = 120^{\circ}$ (Fig. 3c and 3d). As shown in Fig. 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 (Fig. 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° (Fig. 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 Fig. 3i) can also be found. Therefore, as depicted in Fig. 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. Afterwards, 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 can also be observed at the annealing temperature of 453 K, and the ratio of the chiral Au-alkynyl networks to the honeycomb Au-alkynyl networks is 7:1. When the sample was further annealed to 473 K, many organometallic fragments could be found in the gap between the blue and white dashed lines (Fig. 3e), thereby suggesting that the chiral networks might be fragmented and then transform into the honeycomb networks. The magnified image in Fig. 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 Aualkynyl networks was 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 (Fig. S5 in the Supporting Information). 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 (Fig. 3g). Note that the honeycomb Au-alkynyl networks formed on the Au(111) surface represent multiple domains (20–55 nm², Fig. 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 Fig. 3h shows the detailed structure of the honeycomb Au-alkynyl networks with a unit cell of $a = b = 21.3 \pm 0.8$ Å, $\theta = 120^{\circ}$, which is in agreement with that obtained in a

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previous study.¹¹ 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 -57.0 to -90.1 meV (Fig. 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 Fig. S8). Thus, hightemperature annealing is not a good way to convert current organometallic networks into 2D covalent networks.



Assembly

Rotation and Bonding

Chirality Propagation

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 on Au(111) annealed at 473 K. (g, h) 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 the green dashed circles. Scanning parameters (a–i): U = -1.0 V, I = 0.1 nA.

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 (Fig. 4a, blue line). By contrast, breaking the Aualkynyl 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 (Fig. 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 breaking/forming 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 (Fig. 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 (Fig. 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).



Figure 4. Breaking of metal-alkynyl bonds on Ag(111) and Au(111) surfaces. a) Breaking of metal-alkynyl bond without the assistance of a chlorine atom. b) Breaking of metal-alkynyl bond with the assistance of a chlorine atom. The brown and blue lines represent the reactions occurring on Au(111) and Ag(111) surfaces, respectively. Top and side views of the initial state (IS), transition state (TS), and final state (FS) are for the reaction on Au(111).

CONCLUSION

In summary, the stepwise growth mechanism of organometallic metal-alkynyl networks, utilizing the tCEB precursor with a threefold 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 largescale 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. Detailed descriptions of experimental and theoretical procedures, and additional STM and DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Stepwise Growth Mechanism