

Direct Formation of C–C Triple-Bonded Structural Motifs by On-Surface Dehalogenative Homocouplings of Tribromomethyl-Substituted Arenes

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Abstract: On-surface synthesis shows significant potential in constructing novel nanostructures/nanomaterials, which has been intensely studied in recent years. The formation of acetylenic scaffolds provides an important route to the fabrication of emerging carbon nanostructures, including carbyne, graphyne, and graphdiyne, which feature chemically vulnerable *sp*-hybridized carbon atoms. Herein, we designed and synthesized a tribromomethyl-substituted compound. By using a combination of high-resolution scanning tunneling microscopy, non-contact atomic force microscopy, and density functional theory calculations, we demonstrated that it is feasible to convert these compounds directly into C–C triple-bonded structural motifs by on-surface dehalogenative homocoupling reactions. Concurrently, *sp*³-hybridized carbon atoms are converted into *sp*-hybridized ones, that is, an alkyl group is transformed into an alkynyl moiety. Moreover, we achieved the formation of dimer structures, one-dimensional molecular wires, and two-dimensional molecular networks on Au(111) surfaces, which should inspire further studies towards two-dimensional graphyne structures.

On-surface synthesis has been a research area of intense interest in recent years, and various chemical reactions have been studied and achieved on different surfaces. Generally speaking, most of the on-surface chemical reactions follow different reaction pathways from their counterparts in solution owing to the catalytic effect of the surface.^[1–4] As a result, many unexpected reactions have been achieved on

different surfaces.^[5–9] Thus on-surface synthesis demonstrates remarkable potential in the fabrication of novel nanostructures/nanomaterials that still remain challenging to be obtained by traditional synthetic methods. For instance, carbon materials, including fullerenes, graphene, graphene nanoribbons, single-chirality carbon nanotubes, and metalated carbyne, as well as different hydrocarbons have been successfully fabricated by such on-surface synthetic strategies.^[10–14]

Remarkably, the formation of acetylenic scaffolds (i.e., *sp*-hybridized carbon structures) has been attempted on surfaces, and has been advanced recently.^[15–19] The demand for acetylenic scaffolds is due to the emergence of carbon nanostructures/nanomaterials, such as one-dimensional linear carbon (i.e., carbyne) and two-dimensional graphyne/graphdiyne structures, which contain *sp*-hybridized carbon atoms. However, scientific and technological advances made with these interesting carbon nanomaterials are significantly impeded by the high chemical activity of *sp*-hybridized carbon atoms. On-surface C–X bond activation followed by a C–C coupling provides a relatively efficient route to the synthesis of acetylenic linkages.

Through dehydrogenative or dehalogenative homocoupling reactions of terminal alkynes and alkynyl bromides, various structures containing diyne motifs have been formed on surfaces.^[15–19] However, the further functionalization of these molecular precursors with additional alkynyl groups to form carbon allotropes (e.g., graphdiyne) is hampered by the increasing instability of the precursors (e.g., hexaethynylbenzene). Thus it is of utmost importance to explore new strategies with the aim of forming acetylenic linkages on surfaces.

Thus far, most of the halide precursors employed for dehalogenative homocouplings contained only one halogen attached to a carbon atom. Very recently, we introduced a new on-surface reaction that is based on dehalogenative homocouplings of alkenyl *gem*-dibromides (i.e., generating two unpaired electrons), in which cumulene motifs with newly formed C–C double bonds were consequently constructed.^[20] In light of this previous work, we now investigated on-surface dehalogenative homocouplings of tribromomethyl-substituted compounds (i.e., generating three unpaired electrons) to explore the possibility of directly forming C–C triple bonds from *sp*³-hybridized carbon atoms. As shown in Figure 1, we have designed and synthesized a molecule functionalized with a tribromomethyl group (TBP; see the Supporting Information for details of the synthesis). By a combination of high-

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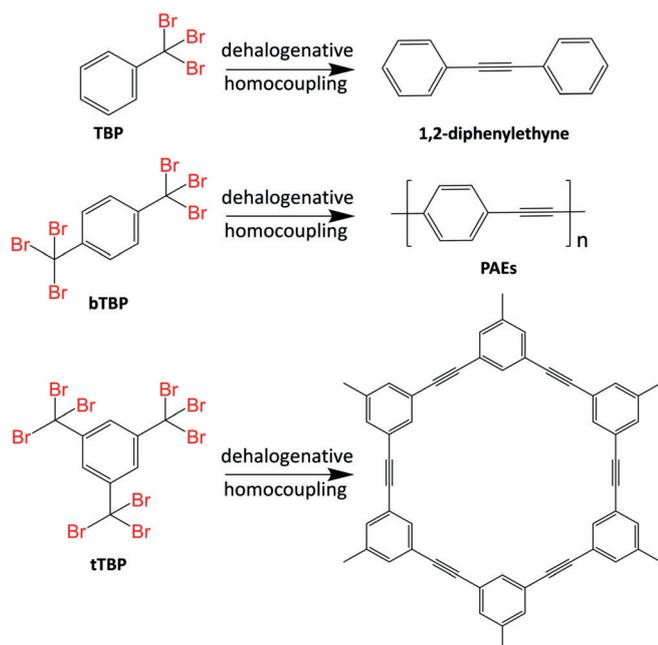


Figure 1. Dehalogenative homocouplings of TBP, bTBP, and tTBP molecules.

resolution scanning tunneling microscopy (STM) imaging, non-contact atomic force microscopy (nc-AFM) imaging, and density functional theory (DFT) calculations, we investigated dehalogenative homocouplings of these TBP molecules on a Au(111) surface. Interestingly, the 1,2-diphenylethyne products (i.e., with a C–C triple bond) were formed at room temperature on the surface, which was confirmed by high-resolution STM and nc-AFM imaging. A step further, we functionalized other molecular precursors with two and three tribromomethyl groups (bTBP and tTBP; see the Supporting Information for details of the synthesis), with the aim of extending our strategy to form one-dimensional molecular chains and two-dimensional networks. By making use of these dehalogenative homocoupling reactions, we successfully fabricated a linear graphyne wire, namely a poly(arylene ethynylene) (PAE),^[21] and also 2D network structures on the Au(111) surface (Figure 1). We thus demonstrate the versatility of on-surface dehalogenative C–C homocoupling reactions and, more importantly, provide an alternative strategy for the transformation of compounds containing C–C triple bonds into surface nanostructures.

After the deposition of TBP molecules on a Au(111) surface at room temperature, we observed ordered molecular arrays by STM (Figure 2a). A closer examination of the image revealed that the island was composed of dumbbell-shaped molecular motifs and encircled bright spots. The dumbbell-shaped motifs were orientated along the [11-2] direction of the Au(111) surface. According to previous studies,^[22–24] the bright round spots can be attributed to dissociated bromine atoms, which are stabilized by weak hydrogen bonds to phenyl groups of the molecules. A close-up STM image (Figure 2b) revealed that the dumbbell-shaped molecular motif is approximately 1.1 nm long, which agrees well with the length of the expected product 1,2-diphenyle-

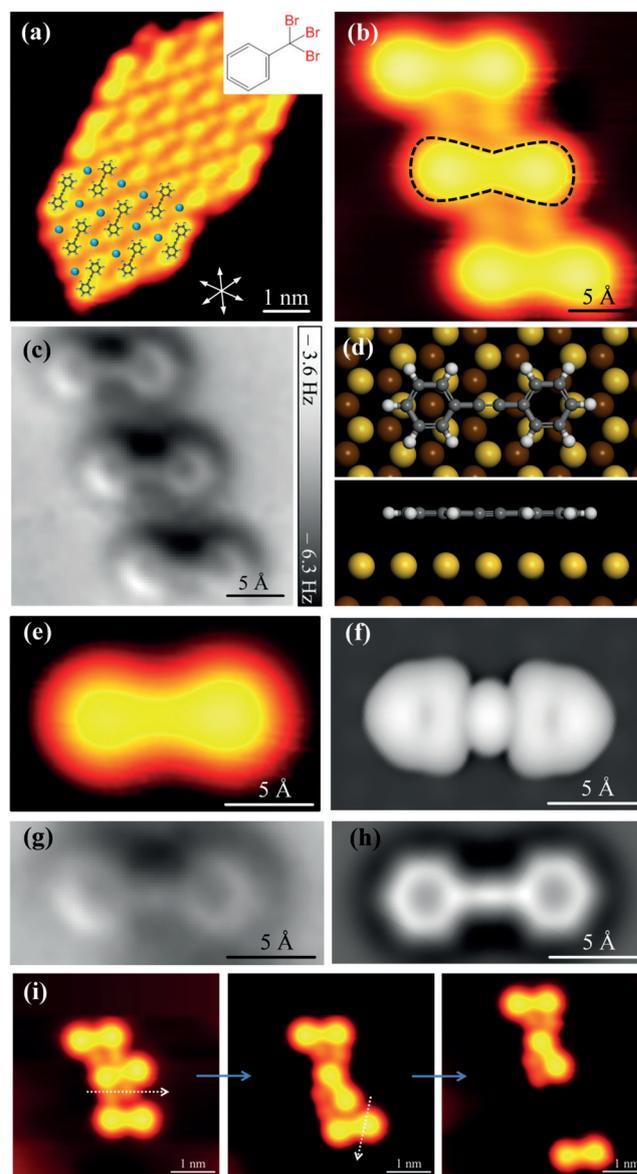


Figure 2. a) Large-scale STM image of the 1,2-diphenylethyne product self-assembled on the Au(111) surface (with overlaid molecular structures; $V = 500$ mV, $I = 70$ pA). The blue balls denote the detached Br atoms. White arrows represent the directions of the close-packed lattice of the Au(111) surface. b) Close-up STM image of the 1,2-diphenylethyne product ($V = 500$ mV, $I = 30$ pA) and c) the corresponding nc-AFM image recorded with a CO-functionalized tip. The black contour in (b) denotes the dimer structure. d) Top and side views of the DFT-optimized model of the 1,2-diphenylethyne product structure on Au(111). e) High-resolution STM image and f) the corresponding STM simulation of the 1,2-diphenylethyne structure. g) nc-AFM image and h) the corresponding AFM simulation of the 1,2-diphenylethyne structure. i) A series of STM images showing the lateral STM manipulation processes.

thyne from the TBP molecular precursors. To further identify the atomic-scale structure, we performed nc-AFM experiments as shown in Figure 2c. The dumbbell-shaped molecular motif is composed of two phenyl groups linked by a linear backbone. The enhanced contrast in the middle of the linear

bond can be assigned to the C–C triple bond.^[5,25] Moreover, we performed extensive DFT calculations to identify the atomic-scale structures on the surface as shown in the Figure 2d, and we calculated the adsorption of the 1,2-diphenylethyne product on Au(111). Based on a detailed comparison of the STM^[18,19] and nc-AFM experimental morphologies and dimensions with the molecular model, we assigned the dumbbell-like molecular motif to the 1,2-diphenylethyne product formed by dehalogenative homocoupling of two TBP molecules on the surface.

To further confirm the formation of the C–C triple-bonded structural motif, we also calculated the corresponding STM image and a constant-height nc-AFM image of 1,2-diphenylethyne on Au(111) as shown in Figure 2f,h,^[26] respectively; these agree well with the experimental data (Figure 2e,g). Moreover, lateral STM manipulations were performed to validate the robustness of the formed products as presented in Figure 2i. After a series of STM manipulations, the formed 1,2-diphenylethyne molecule always moved as a whole and remained intact. Therefore, we concluded that the direct formation of C–C triple-bonded 1,2-diphenylethyne molecules had been achieved by the dehalogenative homocoupling of TBP molecular precursors on the surface.

In view of the successful formation of C–C triple bonds from sp^3 -hybridized carbon atoms, we further functionalized the TBP molecule with an additional tribromomethyl group to give bTBP (Figure 3a), with the aim of forming one-dimensional molecular chains featuring C–C triple bonds. As shown in Figure 3a, after deposition of bTBP molecules on a Au(111) surface held at room temperature and further annealing of the sample at 430 K, individual chain structures (surrounded by Br atoms) were formed as expected. In the

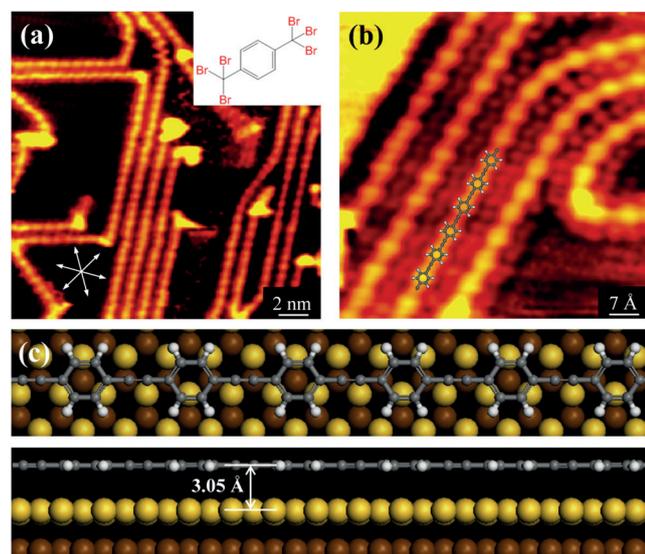


Figure 3. a) Large-scale and b) close-up STM images showing the formation of molecular chains (graphyne wires) after deposition of bTBP molecules on Au(111) held at room temperature followed by annealing to about 430 K. The equally scaled DFT-relaxed model is superimposed on the STM topography. c) Top and side views of the DFT-optimized model of the molecular wire on Au(111). White arrows represent the directions of the close-packed lattice of the substrate.

close-up image shown in Figure 3b, we clearly resolved the chain structure with alternating acetylenic linkages and phenylene groups. We then optimized the structural model of the C–C coupled molecular chain on Au(111) as shown in Figure 3c. The equally scaled structural model was overlaid on the STM image (Figure 3b), and a good agreement in both dimension and morphology was again achieved. It should be noted that we have successfully formed a graphyne wire (i.e., a kind of poly(arylene ethynylene) molecular chain) through dehalogenative C–C couplings of the predesigned molecular precursor bTBP, in analogy to the previously reported on-surface formation of graphdiyne wires.^[18]

Next, to explore the generality of the formation of acetylenic scaffolds (i.e., C–C triple-bonded motifs) in two-dimensional network structures by such on-surface syntheses, we further functionalized the TBP molecule with two additional tribromomethyl groups to give tTBP (Figure 4a), with

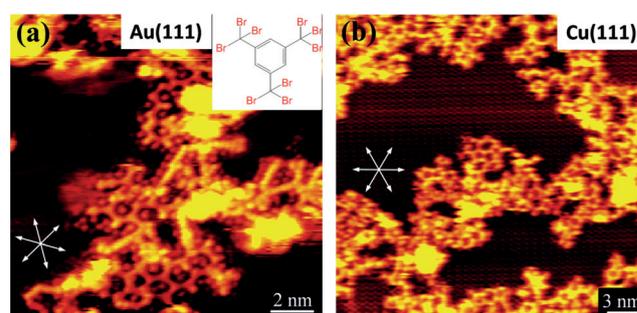


Figure 4. Large-scale STM images showing the formation of the molecular network after deposition of tTBP molecules on a) Au(111) and b) Cu(111) held at room temperature followed by annealing to approximately 500 and 430 K, respectively. White arrows represent the directions of the close-packed lattice of the substrate.

the aim of forming two-dimensional molecular networks. Similarly, after deposition of tTBP molecules on Au(111) at room temperature followed by annealing at approximately 500 K, we also observed some patches of network structures (Figure 4a). However, owing to the large amount of detached Br atoms on the surface, the network cannot grow into a more ordered and larger structure. We also carried out the tTBP experiment on Cu(111). As shown in Figure 4b, similarly, we mainly observed patchy network structures on Cu(111). Thus we have demonstrated that it is possible to form C–C triple-bonded network structures on surfaces as well even though the reaction conditions (getting rid of the Br atoms on the surface) have yet to be optimized towards the fabrication of more ordered 2D network structures. It should be noted that the formation of the molecular wires and networks was not as efficient as that of the dimer structure on the surface. Therefore, post-annealing of the sample is needed to improve the quality of the formed structures. This is also in line with our previous work on the formation of diyne wires and networks on Au(111).^[19]

In conclusion, we have demonstrated the feasibility of directly forming C–C triple-bonded structural motifs by the dehalogenative homocoupling of tribromomethyl-substituted

compounds on surfaces. These processes were studied by high-resolution UHV-STM and nc-AFM imaging combined with DFT calculations. Notably, we have converted sp^3 -hybridized carbon atoms into sp -hybridized ones in this process, as alkyl groups are transformed into alkynyl moieties. This finding demonstrates the possibility of changing the hybridization states of carbon atoms by a multi-dehalogenation process at one carbon site followed by subsequent C–C coupling. This strategy may shed light on the fabrication of novel carbon nanostructures with acetylenic scaffolds from pre-designed molecular precursors. We also obtained graphyne-like molecular wires by such an on-surface synthesis strategy, and are now working on the design and synthesis of molecular precursors towards the formation of two-dimensional graphyne structures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes · dehalogenative homocoupling · non-contact atomic force microscopy · scanning tunneling microscopy · surface chemistry

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