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Direct formation of C-C triple bonded structural motifs by on-surface dehalogenative homocoupling of tribromomethyl molecules

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Abstract: On-surface synthesis shows significant potential in constructing novel nanostructures/nanomaterials, which has been intensely studied over the recent years. The formation of acetylenic scaffoldings provides an important route to the fabrication of emerging carbon nanostructures including carbyne, graphyne and graphdiyne, which involve the chemically vulnerable *sp*-hybridized carbons. Herein, we designed and synthesized a tribromomethyl group, by using the combination of high-resolution scanning tunneling microscopy and non-contact atomic force microscopy imaging and density functional theory calculations, we demonstrated that it is feasibleto achievethe direct formation of C-C triple bonded structural motifs via on-surface dehalogenative homocoupling reactions. Correspondingly, we are able to convert the sp^3 hybridized state to *sp* hybridized state of carbon atoms, *i.e.*, from an alkyl group to an alkynyl one. Moreover, we successfully achieved the formation of dimer structures, one-dimensionalmolecular wires and two-dimensional molecular networks onAu(111) surface,which would inspire further studies towards the 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 solutions, due to the catalytic effect of the surfaces.[1-4] As a result, lots of unexpected reactions have been surprisingly achieved on different surfaces.[5-9] Thus, on-surface synthesis demonstrates remarkable potential to fabricate novel nanostructures/nanomaterials which still remain challenging 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 an on-surface synthesis strategy.[10-14]

Remarkably, the formations of acetylenic scaffoldings (*i.e.*, *sp*-hybridized carbon structures) have been attempted on surfaces and advanced recently.[15-19] The demand for the formation of acetylenic scaffoldings comes from the fabrication of emerging carbon nanostructures/nanomaterials such as one-dimensional linear carbons (*i.e.*, carbyne) and two-dimensional graphyne/graphdiyne structures, which involve *sp*-hybridized carbons. However, scientific and technological advances made on these interesting carbon nanomaterials are significantly impeded due to the high chemical activity of *sp*-hybridized carbons. On-surface C-X bond activations and following C-C couplings provide a relatively efficient route to incorporating acetylenic linkages.

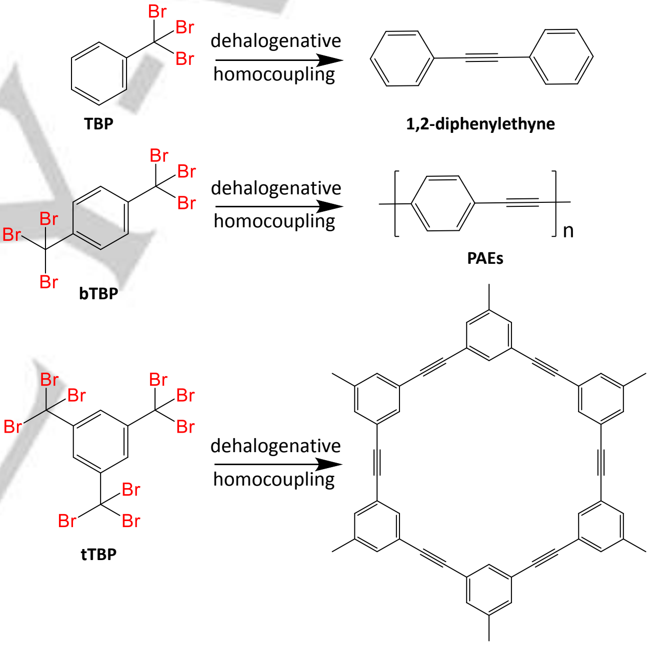

Figure 1.Schematic illustration of dehalogenative homocouplings of TBP, bTBP, and tTBP molecules.

Through dehydrogenative or dehalogenativehomocouplings of terminal alkynes and alkynyl bromides, various structures involving diyne motifs are formed on surfaces.[15-19] While, further functionalizing the molecular precursors with more alkynyl groups to form carbon allotropes (*e.g.*, graphdiyne) is hampered due to the increasing instability of the precursors (*e.g.*, hexaethynyl benzene). Thus, it is of utmost importance to explore new strategies with the aim of forming acetylenic linkages on surfaces.

So far, most of the halide precursors employed for dehalogenative homocouplings have only one halogen attached to a carbon atom. Very recently, we have introduced a new on-surface reaction by dehalogenative homocouplings of alkenyl *gem*-dibromides (*i.e.*, generating two unpaired electrons), in which cumulene motifs with newly formed C-C double bonds are consequently constructed.[20] In light of this previous work, we now try to investigate on-surface dehalogenative homocouplings of tribromomethyl groups (*i.e.*, generating three unpaired electrons) to

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explore the possibility of direct formation of C-C triple bonds from sp^3 hybridized carbons. As shown in Figure 1, we have designed and synthesized a molecule functionalized with the tribromomethyl group (named TBP, synthesis details are shown in SI). From the interplay of high-resolution scanning tunneling microscopy (STM) imaging, non-contact atomic force microscopy imaging (nc-AFM) and density functional theory (DFT) calculations, we have investigated dehalogenative homocouplings of TBP molecules on the Au(111) surface. Interestingly, it is found that the formation of 1,2-diphenylethyne products (*i.e.*, involving C-C triple bonds) occurs at room temperature (RT) on the surface, which is verified by the high-resolution STM and nc-AFM imaging. A step further, we have functionalized the other molecular precursors with two and three functional groups (named bTBP and tTBP, synthesis details are shown in SI) with the aim of extending the strategy to form one-dimensional molecular chains and two-dimensional networks. By activating the dehalogenative homocoupling reactions, we have successfully fabricated a linear graphyne wire, which belongs to poly(aryleneethynylene)s (PAEs),[21]and also 2D network structures on the Au(111) surface (*cf.* Figure 1). This study exhibits the versatility of on-surface dehalogenative C−C homocoupling reactions, and more importantly, it provides an alternative strategy for the involvement of C-C triple bonds into surface nanostructures.

After the deposition of TBP molecules on Au(111) at room temperature (RT), we observed ordered molecular arrays as shown in the STM image (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 orientated along the [11-2] direction of the Au(111) surface. According to the previous studies,[22-24] the round bright spots can be attributed to dissociated bromine atoms and stabilized the molecules by forming weak hydrogen bonds on the surface. Close-up STM image (Figure 2b) revealed that the length of the dumbbell-shaped molecular motif is approximately 1.1 nm, which agreed well with the length of the expected product of 1,2-diphenylethyne from the TBP molecular precursors. To further identify the atomic scale structure, we perform nc-AFM experiments as shown in Figure 2c. The dumbbell-shaped molecular motif is composed of two phenyls linked by alinearbackbone. An enhanced contrast in the middle of the linear bond can be assigned to the C-C triple bond.[5,25] Moreover, we perform extensive DFT calculations to identify the atomic-scale structures on the surface as shown in the Figure 2d, where we calculated the adsorption of the 1,2-diphenylethyne product on Au(111). From a detailed comparison of the STM[18,19] and nc-AFM experimental morphologies and dimensions with the molecular model, we identify that the dumbbell-like molecular motif should be assigned to the 1,2-diphenylethyne product formed by dehalogenative homocoupling of two TBP molecules on the surface.

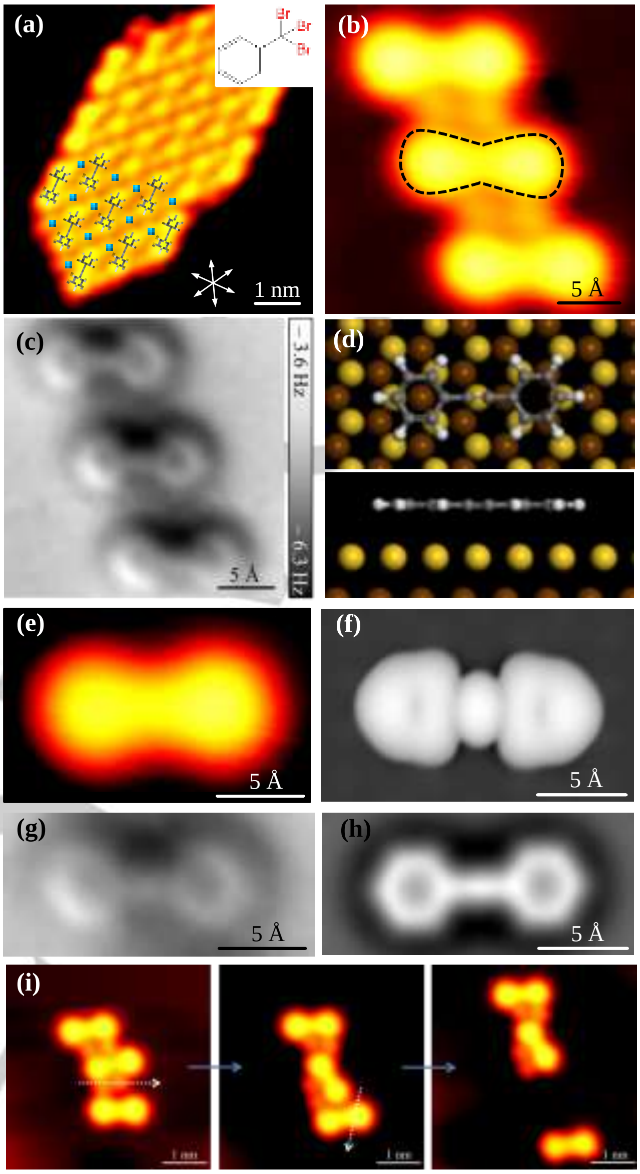

Figure 2. (a) Large-scale STM image of the 1,2-diphenylethyne product self-assembled on the Au(111) surface (with overlaid molecular structures) (V = 500 mV, I = 70pA). The blue balls denotethe detached Br atoms. White arrows represent the close-packed lattice directions of the Au(111) surface. (b) Close-up STM image of the 1,2-diphenylethyne product (V = 500 mV, I = 30 pA) and (c)the corresponding nc-AFM image recorded by CO-functionalized tip ($f_0 \approx$ 40.7kHz, oscillation amplitude A ≈ 100 pm, quality factor Q ≈ 5.6×10^4). 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 onAu(111). (e) High-resolution STM image and (f) the corresponding STM simulation ofthe 1,2-diphenylethyne structure. (g) nc-AFM image and (h) the corresponding AFM simulation of the 1,2-diphenylethynestructure. (i) A series of STM images showing the lateral STM manipulation processes.

To further verify the formation of the C-C triple bonded structural motif, we have also calculated the corresponding STM image and the constant-height nc-AFM image of the 1,2-diphenylethyne on Au(111) as shown in Figure 2f and 2h,[26] respectively, which correspond well with the experimental data (cf. Figure 2e and 2g). Moreover, lateral STM manipulations have been 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

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remained intact. Therefore, we concluded that the direct formation of C-C triple bonded 1,2-diphenylethyne molecules has been achieved by dehalogenative homocoupling of TBP molecular precursors on the surface.

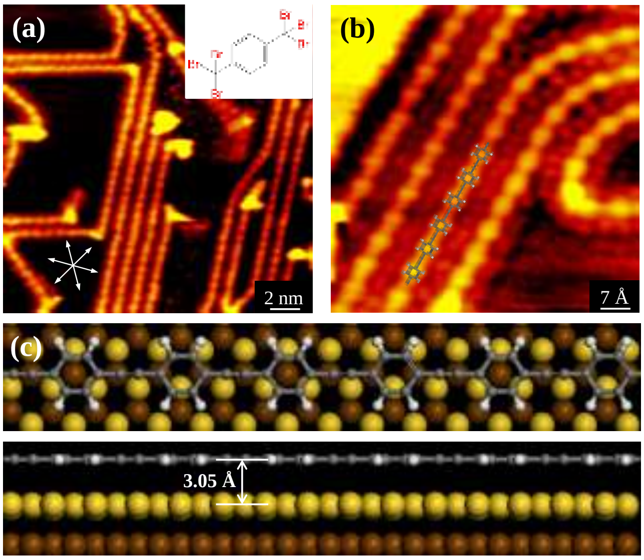

Figure 3.(a) Large-scale and (b) close-up STM images showing the formation of the molecular chains (i.e.graphyne wires) after deposition of bTBP molecules on Au(111) held at RT followed by annealing to ~430 K. The equally scaled DFT-relaxed model is overlaid on the STM topography. (c) Top and side views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

In view of the successful formation of the C-C triple bond from the *sp*^{3} hybridized carbon, we have further functionalized the TBP molecule with an additional tribromomethyl group, named bTBP molecule (as shown in Figure 3a), with the aim of forming one-dimensional molecular chains incorporating C-C triple bonds. As shown in Figure 3a, after deposition of bTBP molecules on Au(111) held at RT and further anneal the sample to 430K, expectedly, individual chain structures (surrounded by Br atoms) are formed. From the close-up image shown in Figure 3b, we could clearly resolve the chain structure with alternating acetylenic linkages and phenyl 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 is overlaid on the STM image (Figure 3b), where a good agreement in both dimension and morphology is also achieved. It is worthy to note that through the dehalogenative C-C couplings of the predesigned molecular precursor bTBP, we have successfully formed a graphyne wire (*i.e.*, a kind of poly(aryleneethynylene) molecular chain), which is in analogy to the previously reported graphdiyne wire on the surface.[18]

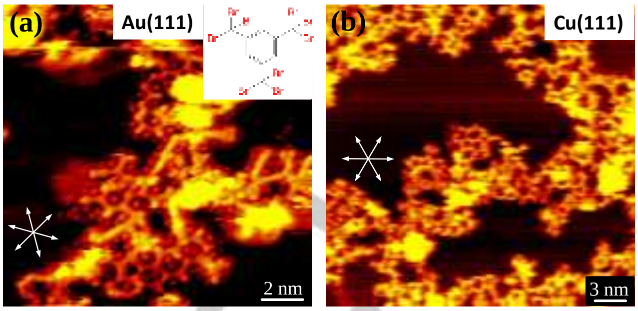

Figure 4. Large-scale STM images showing the formation of the molecular network after deposition of tTBP molecules on (a) Au(111) and (b) Cu(111) held at RT followed by annealing to ~500 K and ~430 K, respectively. White arrows represent the close-packed directions of the substrate.

A step further, to explore the generality of the formation of acetylenic scaffoldings (*i.e.*, C-C triple bonded motifs) in two-dimensional network structures by such an on-surface synthesis strategy, we have further functionalized the TBP molecule with two additional tribromomethyl groups, named tTBP molecule (as shown in Figure 4a), with the aim of forming two-dimensional molecular networks. Similarly, after deposition of tTBP molecules on Au(111) at RT followed by annealing to ~ 500K, we have also observed some patches of network structures as shown in Figure 4a. However, due to a large amount of detached Br atoms on the surface, the network is hampered to grow into a more ordered and larger structure. We have also carried out the tTBP experiment on Cu(111). As shown in Figure 4b, similarly, we have mainly observed some patches of network structures on Cu(111).Thus, we demonstrate that it is possible to form the C-C triple bonded network structure on surfaces as well, though more challenging conditions (getting rid of the Br atoms from the surfaces) have yet to be regulated towards fabrication of more and more ordered 2D network structures. Note that the formation of the aimed molecular wires and networks are not as efficient as that of the dimer structure on the surface. So, post-annealing of the sample is needed to achieve the formed structures with a higher quality. This is also in line with our previous work on the formation of diyne wires and networks on Au(111).[19]

In conclusion, from high-resolution UHV-STM and nc-AFM imaging combined with DFT calculations, we have demonstrated the feasibility of the direct formation of C-C triple bonded structural motifs by dehalogenative homocoupling of tribromomethyl molecules on surfaces. Notably, in this case, we have converted the *sp*^{3} hybridized state to *sp* hybridized state of carbon atoms, *i.e.*, from an alkyl group to an alkynyl one. This finding thus demonstrates the possibility of converting hybridization states of carbon atoms by a multi-dehalogenation process at one carbon site followed by the subsequent C-C coupling. Thus, this strategy may shed light on the fabrication of novel carbon nanostructures with acetylenic scaffoldings from pre-designed molecular precursors. Practically, we have formed graphyne-like molecular wires by such an on-surface synthesis strategy, and inspired from this, design and synthesis of molecular precursors towards the formation of two-dimensional graphyne structures are underway.

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Keywords: Dehalogenativehomocoupling • scanning tunneling microscopy• non-contact atomic force microscopy • acetylenic scaffolding • surface chemistry

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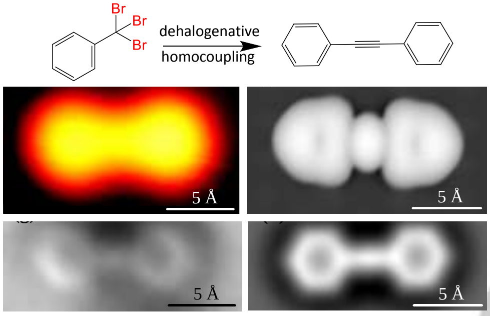
COMMUNICATION

We have demonstrated the feasibility of direct formation of C-C triple bonded structural motifs by dehalogenative homocoupling of tribromomethyl molecules on surfaces.



Qiang Sun, XinYu, MeilingBao, Mengxi Liu, Jinliang Pan, ZeqiZha, Liangliang Cai, Honghong Ma, Chunxue Yuan, XiaohuiQiu, Wei Xu**

Page No. – Page No.

Direct formation of C-C triple bonded structural motifs by on-surface dehalogenative homocoupling of tribromomethyl molecules