

Dehalogenative Homocoupling of Terminal Alkynyl Bromides on Au(111): Incorporation of Acetylenic Scaffolding into Surface Nanostructures

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(5) Supporting Information

ABSTRACT: On-surface C–C coupling reactions of molecular precursors with alkynyl functional groups demonstrate great potential for the controllable fabrication of low-dimensional carbon nanostructures/nanomaterials, such as carbyne, graphyne, and graphdiyne, which demand the incorporation of highly active sp-hybridized carbons. Recently, through a dehydrogenative homocoupling reaction of alkynes, the possibility was presented to fabricate surface nanostructures involving acetylenic linkages, while problems lie in the fact that different byproducts are inevitably formed when triggering the reactions at elevated temperatures. In this work, by delicately designing the molecular precursors with terminal alkynyl bromide, we introduce the dehalogenative homocoupling reactions on the surface. As a result, we successfully achieve the formation of dimer structures, one-dimensional molecular wires and two-dimensional molecular networks with acetylenic scaffoldings on an inert Au(111) surface, where the unexpected C–Au–C organometallic inter-

mediates are also observed. This study further supplements the database of on-surface dehalogenative C–C coupling reactions, and more importantly, it provides us an alternative efficient way for incorporating the acetylenic scaffolding into low-dimensional surface nanostructures.

KEYWORDS: acetylenic scaffolding, on-surface synthesis, scanning tunneling microscopy, C–C homocoupling, surface chemistry

he formation of acetylenic scaffoldings provides an important route to fabricate emerging carbon nanostructures/ nanomaterials. Remarkably, a variety of emerging lowdimensional carbon nanomaterials with predicted extraordinary physicochemical properties, including carbyne, graphyne, and graphdiyne, could be envisioned due to the involvement of the sp-hybridized carbons.^{1–3} Recently, on-surface synthesis has been rapidly advanced with the aim of fabricating covalently interlinked low-dimensional nanostructures, and a number of well-known chemical reactions 4^{-10} and even some unprecedented ones¹¹⁻¹⁵ have been explored on different metal surfaces. As a result, various carbon or carbon-rich nanostructures have been successfully constructed on surfaces, such as fullerene,¹⁶ graphene nanoribbons,^{17–23} nanographene,²⁴ polyphenylene chains,^{13,25} and other low-dimensional nanostructures.²⁶⁻²⁸ The C-C homocoupling reaction of reactants with predefined C-X groups (X stands for hydrogen and halogens) has proven to be one of the most efficient ways for controllable formation of different carbon scaffoldings, in which dehalogenative homocouplings have been mainly limited to aryl halides (sp²-carbon), that is, Ullmann coupling.^{10,26} More recently, dehalogenative homocouplings of alkyl (sp³-carbon) and alkenyl (sp²-carbon) halides have also been demonstrated on surfaces.^{29,30} For the C–H activation, dehydrogenative homocouplings of terminal alkanes (sp³-carbon), alkenes and arenes (both sp²-carbons), and alkynes (sp¹-carbon) have also been recently investigated on surfaces.^{9,12,13,31,32}

Among others, only the dehydrogenative coupling of terminal alkynes could result in the acetylenic linkages. However, situations become complicated for reactions involving terminal alkynes, where diverse products including diynes,^{8,9} organometallic motifs,^{33,34} phenyl groups,^{35,36} and others could be formed on different surfaces,^{9,37} and sometimes byproducts are inevitable when triggering the reaction at elevated temperatures. Generally, from the comparison of on-surface dehydrogenative C–C couplings with dehalogenative ones, the latter ones usually yield higher selectivity and fewer byproducts because the C–X bond cleavage (X typically stands for Br and I) on surfaces is relatively facile. Therefore, it is of general interest to introduce dehalogenative

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Scheme 1. (a) Schematic Illustration of Dehalogenative Homocouplings of BEBP, bBEBP, and tBEP Molecules^{*a*} and (b) Molecular Models of BEBP, bBEBP, and tBEP Molecules (Chemical Names and Definitions are Indicated in the Supporting Information)



^aC-M-C organometallic intermediates are formed after dehalogenations, and C-C coupled acetylenic moieties are finally formed *via* subsequent demetalations.



Figure 1. (a) Large-scale and (b) close-up STM images showing the formation of the C-Au-C organometallic intermediates after deposition of BEBP molecules on Au(111) at RT. The scaled model of the C-Au-C species is overlaid on the corresponding STM topography, and the detached Br atoms are indicated by circles in (b). White arrows represent the close-packed directions of the substrate. (c) Line scan profile with the measured dimension of the C-Au-C species shown in (b). The DFT optimized model with the theoretical length and the corresponding STM simulation of the C-Au-C species are shown above. (d) Top and side views of the DFT optimized model of the C-Au-C species on Au(111).

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homocouplings of alkynyl (sp¹-carbon) halides as another type of on-surface reaction and, moreover, as a complementary method for fabricating emerging carbon nanostructures involving acetylenic scaffoldings.

In this work, we design and synthesize three organic molecules with one, two, and three alkynyl bromide groups, respectively, as shown in Scheme 1. It thus may allow us to construct a model system for introducing dehalogenative homocouplings of alkynyl bromides on a surface and, more importantly, to explore the feasibility of fabricating nanostructures involving acetylenic scaffoldings. Herein, from the interplay of highresolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we demonstrate that the formations of dimer structures, one-dimensional (1-D) molecular wires and two-dimensional (2-D) molecular networks with acetylenic scaffoldings, are successfully achieved on a Au(111) surface, where the unexpected corresponding C-Au-C organometallic intermediates are also observed. In comparison with dehalogenative C-C homocouplings of other hybridized carbons (e.g., sp²-carbon for Ullmann coupling^{10,26} and sp³-carbon for Wurtz coupling³⁰) on metal surfaces, this study further supplements the database of on-surface C-C coupling reactions by introducing terminal alkynyl bromides (*i.e.*, sp¹-carbon). More importantly, it provides us an alternative and more efficient way for incorporating acetylenic scaffoldings into low-dimensional surface nanostructures.

RESULTS AND DISCUSSION

After deposition of BEBP molecules on Au(111) at room temperature (RT), we observe the formation of ordered islands, as shown in Figure 1a. From the close-up STM image (Figure 1b), we identify that the molecular island consists of building blocks with a rodlike structure and bright protrusions, as highlighted by blue and white contours, respectively. The rod-like structure is composed of two lobes at both ends (which are attributed to the debrominated BEBP molecules) and a single protrusion in the middle (which is assigned to a gold atom). To further identify the atomicscale structure of this rod-like feature, we perform extensive DFT calculations. From a detailed comparison of the experimental morphology and dimensions with the molecular model and the simulated STM image (Figure 1c), we distinguish that the rod-like feature should be assigned to a C–Au–C organometallic species, as shown in Figure 1d. The protrusions between the organometallic species are attributed to the detached bromine atoms, which further stabilize the structure by forming hydrogen bonds.^{38,39}

When the sample was further annealed to ~400 K, ordered island structures were also observed on the surface, as shown in Figure 2a. From the close-up STM image (Figure 2b), we identify that it consists of another kind of rod-like structure, as highlighted by the blue contour. With the knowledge of a thermally induced demetalation process from an organometallic intermediate to a final C-C coupled product for aryl bromides and alkenyl bromides on metal surfaces,^{25,26,29} and also from a detailed comparison of the experimental morphology and dimensions with the DFT optimized molecular model and the simulated STM image (Figure 2c), we distinguish that such a rod-like feature should be assigned to a divne product, as shown in Figure 2d. Note that the transformation from C-Au-C organometallic intermediates to divne products is also corroborated by the fact that a moderate thermal treatment (\sim 370 K) leads to the coexistence of the two different phases, as shown in Figure S1.



Figure 2. (a) Large-scale and (b) close-up STM images showing the formation of the C–C coupled diyne product after the sample was annealed to \sim 400 K. The scaled model is overlaid on the corresponding STM topography, and the Br atoms are indicated by circles in (b). (c) Line scan profile with the measured dimension of the diyne product shown in (b). The DFT optimized model with the theoretical length and the corresponding STM simulation are shown above. (d) Top and side views of the DFT optimized model of the diyne product on Au(111).



Figure 3. (a) Large-scale and (b) close-up STM images showing the formation of the C-Au-C organometallic chains after deposition of bBEBP molecules on Au(111) at RT and slight anneal to 320 K. The scaled model of a C-Au-C chain is overlaid on the corresponding STM topography. (c) Top and side views of the DFT optimized model of the C-Au-C chain on Au(111).



Figure 4. (a) Large-scale and (b) close-up STM images showing the formation of the C–C coupled molecular chains with acetylenic scaffoldings after the sample is annealed to \sim 425 K. The scaled model of a molecular chain is overlaid on the corresponding STM topography. (c) Top and side views of the DFT optimized model of the molecular chain on Au(111).



Figure 5. (a) STM image showing the formation of the C-Au-C organometallic network after deposition of tBEP molecules on Au(111) at RT and slight anneal to 320 K. (b) STM image showing the formation of molecular networks mainly with acetylenic scaffoldings after annealing the sample to ~450 K. (c-e) Close-up STM images of the C-Au-C organometallic network, the mixture of C-Au-C organometallic and C-C coupled motifs, the C-C coupled network, respectively. The scaled models of the corresponding structures are overlaid on the STM topographies. (f,g) Top and side views of the DFT optimized models of the C-Au-C organometallic network and C-C coupled one on Au(111).

It is interesting to note that in comparison with Ullmann coupling on Au(111), where the debromination step typically occurs at elevated temperatures of 370-470 K, 10,17,18 the debromination of alkynyl bromides investigated here occurs even below 150 K determined experimentally, which should be attributed to the intrinsic properties of different hybridized carbons. Moreover, it is usually rare to form organometallic species for dehalogenative or dehydrogenative couplings on Au(111)with the native gold atoms. To our knowledge, there are only limited examples showing the formation of gold-organic hybrids on Au(111) via thermally initiated dehalogenation of aryl halides.^{18,40} Thus, in this study, the formation of C-Au-C organometallic species at RT via the debromination of alkynyl bromides is still unprecedented. The involvement of gold atoms is further supported from large-scale STM images, as shown in Figure S2, where it is clearly seen that after deposition of BEBP molecules on a clean Au(111) surface (Figure S2a) at RT the herringbone reconstruction underneath the molecular islands (i.e., the C-Au-C organometallic intermediates) is lifted (Figure S2b),^{20,40} and after

the surface is annealed at \sim 400 K, when the gold atoms are released from the organometallic species, the herringbone reconstruction is still not restored (Figure S2c).

Since we have successfully formed the diyne moiety through a dehalogenative homocoupling of terminal alkynyl bromide precursors, a step further, we try to demonstrate the feasibility of formation of more complicated surface nanostructures via the same coupling reaction. We then synthesize another two molecular precursors (i.e., bBEBP and tBEP as shown in Scheme 1) with the aim to fabricate 1-D molecular chains and 2-D molecular networks. As shown in Figure 3a, after deposition of bBEBP molecules on Au(111) at RT and slight anneal to 320 K, expectedly, 1-D chains are formed on the surface. From the close-up STM image (Figure 3b), we distinguish that the chain structures are composed of two kinds of alternating protrusions, which are assigned to biphenyl groups and gold atoms. The detached bromine atoms are aligned between the chains. Based on the above assignment, we construct the molecular model of the C-Au-C organometallic chain and perform DFT calculations, as shown in Figure 3c. The equally scaled model of an organometallic chain is overlaid on the STM image (Figure 3b), where a good agreement in both dimension and topography is achieved.

Further annealing the sample to ~425 K results in the formation of C–C coupled molecular chains with acetylenic linkages, as shown in Figure 4a,b. From the close-up STM (Figure 4b) and in comparison with the organometallic chain (Figure 3b), we identify that the dot protrusions between biphenyl groups disappear, which implies the release of gold atoms. We then construct the molecular model of the C–C coupled chain and perform DFT calculations, as shown in Figure 4c. The equally scaled model is overlaid on the STM image (Figure 4b), where a good agreement in both dimension and topography is also achieved. Note that the fuzzy shapes of the molecular chains should be attributed to the movement of the molecular chain.

To take the next step toward the synthesis of 2-D carbon allotropes as graphyne and graphdiyne, that is, 2-D networks, we employ the three-fold-symmetric tBEP molecule, as shown in Scheme 1. As shown in Figure 5a, after deposition of tBEP molecules on Au(111) at RT and slight anneal to 320 K, honeycomb networks are formed on the surface. From the close-up STM image (Figure 5c), we identify that the network structures are composed of C-Au-C organometallic linkages, in analogy with the cases of BEBP and bBEBP molecules. The C-Au-C organometallic structure is also supported by the DFT optimized molecular model overlaid on the STM topography (also see Figure 5f). Further annealing the sample to ~450 K results in the formation of C-C coupled molecular networks with acetylenic linkages, as shown in Figure 5b,e. From the close-up STM image (Figure 5e), we distinguish that the gold atoms are released, which is also reflected from the scaled optimized model overlaid on the STM image (also see Figure 5g).

It should also be noted that the demetalation of 2-D organometallic networks is not as efficient as those of the dimer structures of BEBP and 1-D chains of bBEBP, which is reflected from the STM images where the hexagonal structures are not exactly uniform. From the close-up STM image (Figure 5d) and in comparison with the overlaid model, we distinguish that some gold atoms are not released from C–Au–C linkages. We speculate that release of gold atoms is somehow sterically hampered within the networks, in comparison with the dimer structures and 1-D chains, which is also implied by the fact that formation of acetylenic C–C linkages is favored at the periphery of the networks over the inside. The pore sizes of the organometallic network and C–C coupled one are determined to be 23.31 and 18.57 Å, respectively, both of which are consistent with their corresponding experimental data.

CONCLUSION

In conclusion, by combining high-resolution UHV-STM imaging and DFT calculations, we have demonstrated that it is feasible to incorporate acetylenic scaffoldings into surface nanostructures from dimer motifs over 1-D chains to 2-D networks through dehalogenative homocouplings of alkynyl bromides on a Au(111) surface, in which C–Au–C organometallic intermediates are also unexpectedly observed. The findings presented here are of fundamental importance to supplement our understandings of on-surface dehalogenative homocoupling reactions and to provide complementary insights into the on-surface dehydrogenative homocoupling of alkynes. More importantly, it may pave the way for the ultimate goal of fabricating graphyne and graphdiyne^{2,3} that involve sp-hybridized carbons.

MATERIALS AND METHODS

The STM experiments were carried out in a UHV chamber with a base pressure of 1×10^{-10} mbar. The whole system was equipped with a variable-temperature "Aarhus-type" scanning tunneling microscope, ^{41,42} a molecular evaporator, and standard facilities for sample preparation. The metal substrates were prepared by several cycles of 1.5 keV Ar⁺ sputtering followed by annealing, resulting in clean and flat terraces separated by monatomic steps. After the system was thoroughly degassed, the BEBP, bBEBP, and tBEP molecules were sublimated from the molecular evaporator at 290, 328, and 303 K, respectively. 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 typical scanning parameters were as follows: $I_t = \pm 0.5$ –1.0 nA, $V_t = \pm 1000$ –2000 mV.

All of the calculations were performed in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).^{43,44} The projectoraugmented wave method was used to describe the interaction between ions and electrons.^{45,46} We employed the Perdew–Burke–Ernzerhof generalized gradient approximation exchange-correlation functional,⁴⁷ and van der Waals interactions were included using the dispersioncorrected DFT-D2 method of Grimme.⁴⁸ The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were $\leq 0.03 \text{ eV/Å}$ for geometry optimization. The simulated STM image was obtained using the Tersoff–Hamann method,⁴⁹ in which the local density of states was used to approximate the tunneling current.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b03048.

Synthesis details of three molecular precursors and supplementary STM images (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Klappenberger, F.; Zhang, Y. Q.; Bjork, J.; Klyatskaya, S.; Ruben, M.; Barth, J. V. On-Surface Synthesis of Carbon-Based Scaffolds and Nanomaterials Using Terminal Alkynes. *Acc. Chem. Res.* **2015**, *48*, 2140–2150.

(2) Hirsch, A. The Era of Carbon Allotropes. Nat. Mater. 2010, 9, 868-871.

(3) Diederich, F.; Kivala, M. All-Carbon Scaffolds by Rational Design. *Adv. Mater.* **2010**, *22*, 803–812.

(4) de Oteyza, D. G.; Gorman, P.; Chen, Y. C.; Wickenburg, S.; Riss, A.; Mowbray, D. J.; Etkin, G.; Pedramrazi, Z.; Tsai, H.; Rubio, A.; Crommie, M. F.; Fischer, F. R. Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions. *Science* **2013**, *340*, 1434–1437.

(5) Diaz Arado, O.; Monig, H.; Wagner, H.; Franke, J. H.; Langewisch, G.; Held, P. A.; Studer, A.; Fuchs, H. On-Surface Azide–Alkyne Cycloaddition on Au (111). ACS Nano 2013, 7, 8509–8515.

(6) Sun, Q.; Zhang, C.; Li, Z.; Kong, H.; Tan, Q.; Hu, A.; Xu, W. On-Surface Formation of One-Dimensional Polyphenylene through Bergman Cyclization. J. Am. Chem. Soc. **2013**, 135, 8448–8451.

(7) Bebensee, F.; Bombis, C.; Vadapoo, S. R.; Cramer, J. R.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. On-Surface Azide– Alkyne Cycloaddition on Cu (111): Does It "Click" in Ultrahigh Vacuum? *J. Am. Chem. Soc.* **2013**, *135*, 2136–2139.

(8) Zhang, Y. Q.; Kepcija, N.; Kleinschrodt, M.; Diller, K.; Fischer, S.; Papageorgiou, A. C.; Allegretti, F.; Bjork, J.; Klyatskaya, S.; Klappenberger, F.; Ruben, M.; Barth, J. V. Homo-Coupling of Terminal Alkynes on a Noble Metal Surface. *Nat. Commun.* **2012**, *3*, 1286.

(9) Gao, H. Y.; Wagner, H.; Zhong, D.; Franke, J. H.; Studer, A.; Fuchs, H. Glaser Coupling at Metal Surfaces. *Angew. Chem., Int. Ed.* **2013**, *52*, 4024–4028.

(10) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. Nano-Architectures by Covalent Assembly of Molecular Building Blocks. *Nat. Nanotechnol.* **2007**, *2*, 687–691.

(11) Gao, H. Y.; Held, P. A.; Knor, M.; Mück-Lichtenfeld, C.; Neugebauer, J.; Studer, A.; Fuchs, H. Decarboxylative Polymerization of 2, 6-Naphthalenedicarboxylic Acid at Surfaces. *J. Am. Chem. Soc.* **2014**, 136, 9658–9663.

(12) Zhong, D.; Franke, J.; Podiyanachari, S. K.; Blömker, T.; Zhang, H.; Kehr, G.; Erker, G.; Fuchs, H.; Chi, L. Linear Alkane Polymerization on a Gold Surface. *Science* **2011**, *334*, 213–216.

(13) Sun, Q.; Zhang, C.; Kong, H.; Tan, Q.; Xu, W. On-Surface Aryl–Aryl Coupling *via* Selective C–H activation. *Chem. Commun.* **2014**, 50, 11825–11828.

(14) Wiengarten, A.; Seufert, K.; Auwarter, W.; Ecija, D.; Diller, K.; Allegretti, F.; Bischoff, F.; Fischer, S.; Duncan, D. A.; Papageorgiou, A. C.; Klappenberger, F.; Acres, R. G.; Ngo, T. H.; Barth, J. V. Surface-Assisted Dehydrogenative Homocoupling of Porphine Molecules. *J. Am. Chem. Soc.* **2014**, *136*, 9346–9354.

(15) Int Veld, M.; Iavicoli, P.; Haq, S.; Amabilino, D. B.; Raval, R. Unique Intermolecular Reaction of Simple Porphyrins at a Metal Surface Gives Covalent Nanostructures. *Chem. Commun.* **2008**, *13*, 1536–1538.

(16) Otero, G.; Biddau, G.; Sánchez-Sánchez, C.; Caillard, R.; López, M. F.; Rogero, C.; Palomares, F. J.; Cabello, N.; Basanta, M. A.; Ortega, J.; Mendez, J.; Echavarren, A. M.; Perez, R.; Gomez-Lor, B.; Martin-Gago, J. A. Fullerenes from Aromatic Precursors by Surface-Catalysed Cyclodehydrogenation. *Nature* **2008**, *454*, 865–868.

(17) Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Mullen, K.; Fasel, R. Atomically Precise Bottom-Up Fabrication of Graphene Nanoribbons. *Nature* **2010**, *466*, 470–473.

(18) Zhang, H.; Lin, H.; Sun, K.; Chen, L.; Zagranyarski, Y.; Aghdassi, N.; Li, S.; Duhm, Q.; Zhong, D.; Li, Y.; Müllen, K.; Fuchs, H.; Chi, L. On-Surface Synthesis of Rylene-Type Graphene Nanoribbons. J. Am. Chem. Soc. **2015**, 137, 4022–4025.

(19) Chen, Y. C.; De Oteyza, D. G.; Pedramrazi, Z.; Chen, C.; Fischer, F. R.; Crommie, M. F. Tuning the Band Gap of Graphene Nanoribbons Synthesized from Molecular Precursors. *ACS Nano* **2013**, *7*, 6123–6128.

(20) Basagni, A.; Sedona, F.; Pignedoli, C. A.; Cattelan, M.; Nicolas, L.; Casarin, M.; Sambi, M. Molecules-Oligomers-Nanowires-Graphene Nanoribbons: a Bottom-Up Stepwise On-Surface Covalent Synthesis Preserving Long-Range Order. *J. Am. Chem. Soc.* **2015**, *137*, 1802–1808.

(21) Cai, J.; Pignedoli, C. A.; Talirz, L.; Ruffieux, P.; Söde, H.; Liang, L.; Meunier, V.; Berger, R.; Li, R.; Feng, X.; Mullen, K.; Fasel, R. Graphene Nanoribbon Heterojunctions. *Nat. Nanotechnol.* **2014**, *9*, 896–900.

(22) Huang, H.; Wei, D.; Sun, J.; Wong, S. L.; Feng, Y. P.; Neto, A. C.; Wee, A. T. S. Spatially Resolved Electronic Structures of Atomically Precise Armchair Graphene Nanoribbons. *Sci. Rep.* **2012**, *2*, 983.

(23) Han, P.; Akagi, K.; Federici Canova, F. F.; Mutoh, H.; Shiraki, S.; Iwaya, K.; Weiss, P. S.; Asao, N.; Hitosugi, T. Bottom-Up Graphene-Nanoribbon Fabrication Reveals Chiral Edges and Enantio-selectivity. *ACS Nano* **2014**, *8*, 9181–9187.

(24) Treier, M.; Pignedoli, C. A.; Laino, T.; Rieger, R.; Müllen, K.; Passerone, D.; Fasel, R. Surface-Assisted Cyclodehydrogenation Provides a Synthetic Route towards Easily Processable and Chemically Tailored Nanographenes. *Nat. Chem.* **2011**, *3*, 61–67.

(25) Fan, Q.; Wang, C.; Han, Y.; Zhu, J.; Hieringer, W.; Kuttner, J.; Hilt, G.; Gottfried, J. M. Surface-Assisted Organic Synthesis of Hyperbenzene Nanotroughs. *Angew. Chem., Int. Ed.* **2013**, *52*, 4668– 4672.

(26) Wang, W.; Shi, X.; Wang, S.; Van Hove, M. A.; Lin, N. Single-Molecule Resolution of an Organometallic Intermediate in a Surface-Supported Ullmann Coupling Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 13264–13267.

(27) Basagni, A.; Ferrighi, L.; Cattelan, M.; Nicolas, L.; Handrup, K.; Vaghi, L.; Papagni, A.; Sedona, F.; Di Valentin, C.; Agnoli, S.; Sambi, M. On-Surface Photo-Dissociation of C–Br Bonds: towards Room Temperature Ullmann Coupling. *Chem. Commun.* **2015**, *51*, 12593– 12596.

(28) Eichhorn, J.; Strunskus, T.; Rastgoo-Lahrood, A.; Samanta, D.; Schmittel, M.; Lackinger, M. On-Surface Ullmann Polymerization *via* Intermediate Organometallic Networks on Ag (111). *Chem. Commun.* **2014**, *50*, 7680–7682.

(29) Sun, Q.; Cai, L.; Ma, H.; Yuan, C.; Xu, W. The Stereoselective Synthesis of Dienes through Dehalogenative Homocoupling of Terminal Alkenyl Bromides on Cu(110). *Chem. Commun.* **2016**, *52*, 6009–6012.

(30) Sun, Q.; Cai, L.; Ding, Y.; Ma, H.; Yuan, C.; Xu, W. Single-Molecule Insight into Wurtz Reaction on Metal Surfaces. *Phys. Chem. Chem. Phys.* **2016**, *18*, 2730–2735.

(31) Cai, L.; Sun, Q.; Zhang, C.; Ding, Y.; Xu, W. Dehydrogenative Homocoupling of Alkyl Chains on Cu(110). *Chem. - Eur. J.* 2016, 22, 1918–1921.

(32) Sun, Q.; Cai, L.; Ding, Y.; Xie, L.; Zhang, C.; Tan, Q.; Xu, W. Dehydrogenative Homocoupling of Terminal Alkenes on Copper Surfaces: a Route to Dienes. *Angew. Chem., Int. Ed.* **2015**, *54*, 4549–4552.

(33) Sun, Q.; Cai, L.; Wang, S.; Widmer, R.; Ju, H.; Zhu, J.; Li, L.; He, Y.; Ruffieux, P.; Fasel, R.; Xu, W. Bottom-up synthesis of Metalated Carbyne. J. Am. Chem. Soc. **2016**, 138, 1106–1109.

(34) Liu, J.; Chen, Q.; Xiao, L.; Shang, J.; Zhou, X.; Zhang, Y.; Wang, Y.; Shao, X.; Li, J.; Chen, W.; Xu, G. Q.; Tang, H.; Zhao, D.; Wu, K. Lattice-Directed Formation of Covalent and Organometallic Molecular Wires by Terminal Alkynes on Ag Surfaces. *ACS Nano* **2015**, *9*, 6305–6314.

(35) Zhou, H.; Liu, J.; Du, S.; Zhang, L.; Li, G.; Zhang, Y.; Tang, B. Z.; Gao, H. J. Direct Visualization of Surface-Assisted Two-Dimensional Diyne Polycyclotrimerization. *J. Am. Chem. Soc.* **2014**, 136, 5567–5570.

(36) Liu, J.; Ruffieux, P.; Feng, X.; Müllen, K.; Fasel, R. Cyclotrimerization of Arylalkynes on Au (111). *Chem. Commun.* **2014**, *50*, 11200–11203.

(37) Eichhorn, J.; Heckl, W. M.; Lackinger, M. On-Surface Polymerization of 1, 4-diethynylbenzene on Cu (111). *Chem. Commun.* **2013**, 49, 2900–2902.

(38) Sun, Q.; Zhang, C.; Cai, L.; Tan, Q.; Xu, W. Oxygen-Induced Self-Assembly of Quaterphenyl Molecules on Metal Surfaces. *Chem. Commun.* **2014**, *50*, 12112–12115.

(39) Park, J.; Kim, K. Y.; Chung, K. H.; Yoon, J. K.; Kim, H.; Han, S.; Kahng, S. J. Interchain Interactions Mediated by Br Adsorbates in Arrays of Metal–Organic Hybrid Chains on Ag (111). *J. Phys. Chem. C* **2011**, *115*, 14834–11838.

(40) Zhang, H.; Franke, J. H.; Zhong, D.; Li, Y.; Timmer, A.; Arado, O. D.; Mönig, H.; Wang, H.; Chi, L.; Wang, Z.; Müllen, M.; Fuchs, H. Surface Supported Gold-Organic Hybrids: On-Surface Synthesis and Surface Directed Orientation. *Small* **2014**, *10*, 1361–1368.

(41) Besenbacher, F. Scanning Tunnelling Microscopy Studies of Metal Surfaces. *Rep. Prog. Phys.* **1996**, *59*, 1737–1802.

(42) Laegsgaard, E.; Österlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A High-Pressure Scanning Tunneling Microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.

(43) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 48, 13115–13118.

(44) Kresse, G. Furthmüller, Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54, 11169–11186.

(45) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953-17979.

(46) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(47) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(48) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. J. Comput. Chem. 2006, 27, 1787–1799.

(49) Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1985**, *31*, 805–813.