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On-surface dehydro-Diels-Alder reaction of dibromo-bis(phenylethynyl)benzene

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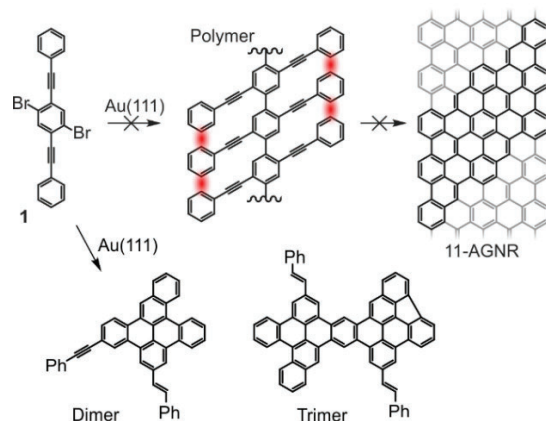
ABSTRACT: On-surface synthesis under ultrahigh vacuum conditions is a powerful tool to achieve molecular structures which cannot be accessed *via* traditional wet chemistry. Nevertheless, only a very limited number of chemical reactions out of the wide variety known from solution chemistry have been reported to proceed readily on atomically flat substrates. Cycloadditions are a class of reactions that are particularly important in the synthesis of *sp*²-hybridized carbon-based nanostructures. Here, we report on a specific type of [4+2] cycloaddition, namely a dehydro-Diels-Alder (DDA) reaction, performed between bis(phenylethynyl)benzene precursors on Au(111). Unlike a Diels-Alder reaction, DDA exploits ethynyl groups to achieve the formation of an extra six-membered ring. Despite its extensive use in solution chemistry for more than a century, this reaction has never been reported to occur on surfaces. The specific choice of our precursor molecule has led to the successful synthesis of benzo- and naphtho-fused tetracene and heptacene products bearing styryl groups, as confirmed by scanning tunneling microscopy and noncontact atomic force microscopy. The two products arise from DDA dimerization and trimerization of the precursor molecules, respectively, and their observation opens perspectives to use DDA reactions as a novel on-surface synthesis tool.

Polycyclic aromatic hydrocarbons (PAHs) are disc-type conjugated molecules consisting of fused benzene rings, which occur in various shapes and sizes, including coronenes, acenes, and larger PAHs that can be regarded as nanographenes.¹⁻³ These materials possess intriguing properties that make them appealing for applications in organic electronics,⁴ as well as for more fundamental studies.⁵ The preparation of PAHs is typically carried out through “planarization” of polyphenylene precursors by photochemical or oxidative cyclodehydrogenation or *via* metal-catalysed or oxidative annulation of tailor-made building blocks.⁶⁻⁹ Cycloaddition reactions are widely used in the synthesis of large PAHs.¹⁰ In this regard, a specific class of [4+2] cycloaddition, namely Diels-Alder reaction where cycloaddition occurs between diene and dienophile, has served as an extremely versatile synthetic protocol to achieve the formation of extra

six-membered rings.^{11,12} An alternative version of the Diels-Alder reaction is the dehydro-Diels-Alder (DDA) reaction where one or both double bonds in the diene component are replaced by a triple bond (Scheme S1).^{13,14} Another distinction of the DDA reaction from the former is that, in most of the studied cases, it proceeds *via* multiple steps by formation of cyclic allenes and migration of hydrogens.

As a complement to conventional synthetic organic chemistry, on-surface synthesis on metal substrates under ultrahigh vacuum conditions has recently emerged as a strong method to achieve novel PAHs that have not been obtained in solution, including e.g. unstable higher acenes, up to undecacene.^{1,10,15} Several chemical reactions traditionally used in solution chemistry have been proven to successfully proceed also on surfaces.¹⁶⁻²⁰ One of the most utilized reactions is the Ullmann-like coupling,^{21,22} or more generally aryl-aryl coupling, which afforded various conjugated polymers as well as two-dimensional covalent organic frameworks on surfaces. This reaction was also combined with intramolecular cyclodehydrogenation to yield atomically precise graphene nanoribbons with varying widths and edge structures, revealing highly intriguing structure-dependent electronic properties.²³⁻²⁶

Scheme 1. On-surface reaction of 1,4-dibromo-2,5-bis(phenylethynyl)benzene (1) and obtained dimer and trimer products.



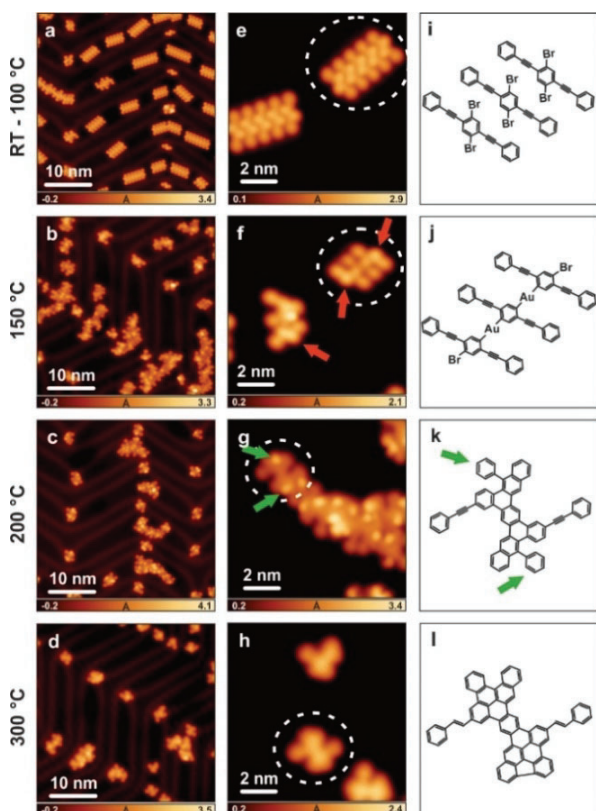


Figure 1. (a-d) STM images of the Au(111) surface after deposition of precursor **1** at RT followed by repeated annealing steps at the indicated temperatures. (e-h) Magnified STM images at different reaction steps. (i-l) Molecular schemes of the structures observed in the STM images. Scanning parameters: (a,e) $I_t=70$ pA, $V_b=0.2$ V; (b) $I_t=30$ pA, $V_b=0.3$ V; (c,g) $I_t=30$ pA, $V_b=1$ V; (d) $I_t=10$ pA, $V_b=1$ V; (f,h) $I_t=70$ pA, $V_b=0.1$ V.

Ullmann-like coupling reactions obviously also encounter limitations in achieving more complex architectures. For instance, only single C-C bonds can be created, while sometimes the formation of an extra ring would be desirable without having to refer to cyclodehydrogenation.^{27,28} Hence, cycloaddition reactions have appeared as a valid on-surface chemistry tool to expand the spectrum of attainable chemical structures.²⁹⁻³⁴

Despite its extensive use in synthetic organic chemistry, the DDA reaction has not been investigated for on-surface processes. During our attempts to synthesize eleven atoms wide armchair GNRs (11-AGNRs) on Au(111) from 1,4-dibromo-2,5-bis(phenylethynyl)benzene (**1**)³⁵ as a precursor, we have observed the formation of dimer- and trimer-like molecules instead of 11-AGNRs (Scheme 1). Here, we demonstrate the dimerization and trimerization of **1**, forming benzo[fg]naphtho[1,2,3-op]tetracene and acenaphtho[4,3,2,1-abicidi]dibenzo[fg,uv]naphtho[3,2,1-lm]heptacene, respectively, through unprecedented on-surface DDA reactions (Scheme 1). The precise chemical structures of the dimer and trimer products are revealed by high-resolution scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM). We discuss a plausible mechanism for the formation of the observed products *via* surface-assisted DDA cycloadditions.

To study the coupling of precursor **1**, we deposited it onto an Au(111) surface held at room temperature (RT) in ultra-high vacuum (UHV). Figure 1a shows an overview STM image of the resulting sample, which consists of intact molecules self-assembled into chains. Halogen-hydrogen interactions are most likely stabilizing this assembly (see Figure S1) which remains unaltered upon annealing up to 100 °C. This observation is in agreement with previous studies where the C-Br bond was found to be stable up to this temperature on Au(111).³⁶ After annealing of the sample to 150 °C, a more disordered assembly of the molecular units appears from the corresponding STM image (Figure 1b). However, some regular moieties are also visible (Figure 1f). The presence of round protrusions between the molecular units suggests the presence of an organometallic structure, as sketched in Figure 1j and S1.^{37,38} Indeed, the measured C-Au distance of 2.4 ± 0.2 Å agrees with previously reported values for organometallic bonding.^{39,40} The first step toward the expected aryl-aryl coupling²² is therefore almost complete at this temperature (some of the bromine atoms are still covalently attached to the precursors, red arrows in Figure 1f).

Annealing the sample to 200 °C produces further modifications in the molecular assemblies (Figure 1c,g). The overall appearance of the surface is characterized by large, ill-defined structures, probably originating from aggregation as well as non-selective coupling reactions (*e.g.* CH activation and lateral fusion) leading to ill-defined oligomers. The formation of the targeted polymer illustrated in Scheme 1, potentially leading to 11-AGNRs, appears to be prevented by steric hindrance between hydrogens (highlighted in red in Scheme 1) and/or unexpected reactions involving the triple bonds that might be activated on the gold surface at 200 °C (*vide infra*). Nevertheless, we also observe molecular objects which can be assigned to dimers and trimers formed from precursor **1**. They possess one or two out-of-plane phenyl rings (green arrows in Figure 1g,k) which are tilted due to the steric hindrance against the planar aromatic cores.

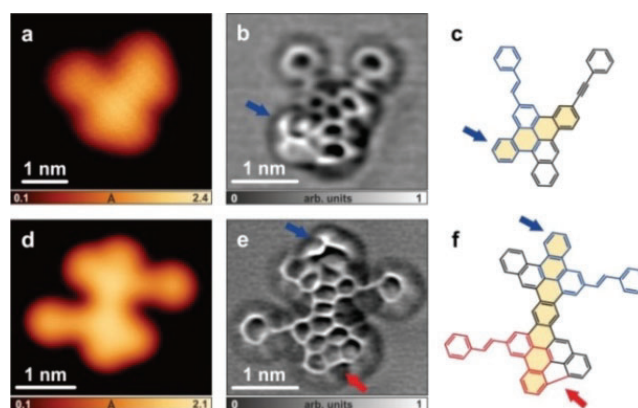
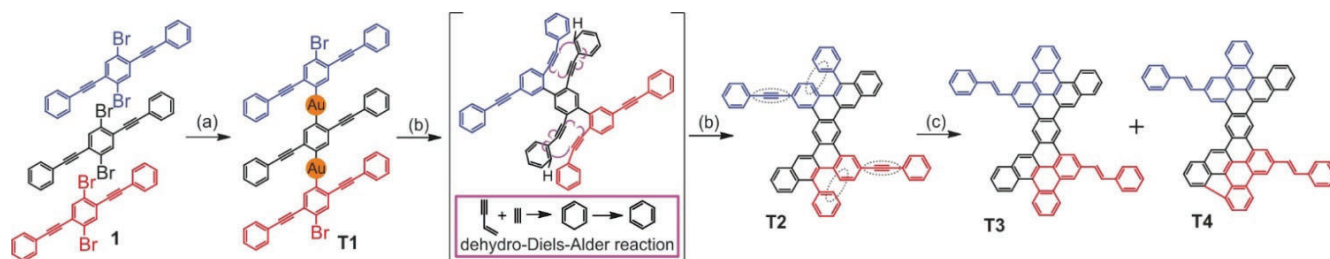


Figure 2. STM images of dimer (a) and trimer (d) products observed after annealing precursor **1** to 300 °C on Au(111). (b,e) Laplace-filtered images of constant-height frequency-shift nc-AFM images performed with CO-functionalized tip. See Figure S2 for the raw data. (c,f) Chemical structures of the observed products. Scanning parameters: (a) $I_t=70$ pA, $V_b=0.1$ V; (d) $I_t=100$ pA, $V_b=-0.02$ V.

Scheme 2. Proposed reaction pathway on Au(111), based on the observed intermediates and final products. Precursor **1 adsorbs intactly on the substrate held at RT and up to 100 °C. (a) Annealing of the surface to 150 °C yields organometallic structures (**T1**). (b) Subsequent heating to 200 °C activates a dehydro-Diels-Alder cycloaddition reaction toward the trimer **T2**. (c) At 300 °C, sequential cyclodehydrogenation and reduction of ethynyl to vinyl take place to form **T3** and **T4**.**



Some of the molecules reach a (nearly) planar conformation after annealing the sample to 300 °C (Figure 1d). We identify two molecular products that are selectively formed with apparently well-defined chemical structures (Figure 1h). Bond-resolved nc-AFM imaging unambiguously elucidates their structures to consist of 44 and 66 carbon atoms, having a benzo- and naphtho-fused tetracene and dibenzo- and dinaphtho-fused heptacene backbones, respectively, which extends laterally with styryl pendent groups (Figure 2). These two products originate from the covalent coupling of two and three monomers, respectively, as sketched with different colors in Figure 2c,f.

Statistical analysis of ~350 molecules on the surface revealed that 9% of them form dimeric products along with 12% of trimeric products. The remaining 79% of the monomers form side products and larger assemblies, which we could not clearly identify because of their increased non-planarity. However, we tentatively ascribe the side products to a non-complete DDA reaction or to different reactions involving ethynyl groups of two or more monomers. On the other hand, the larger assemblies could be aggregates of the products as well as covalently bonded oligomers/polymers originating from non-selective intermolecular couplings. The out-of-plane parts of the tetracene and heptacene cores (blue arrows in Figure 2) are due to steric repulsion between neighboring hydrogens. In contrast, a five-membered ring is observed on the opposite side of the heptacene backbone (red arrows in Figure 2). In this case, the steric overlap between hydrogens at a cove-edge position promoted surface-assisted cyclodehydrogenation, as previously reported.⁴¹

Sequential reaction steps leading to the formation of the observed trimer are proposed in Scheme 2 (see Scheme S3 for the dimer). After debromination of **1** on Au(111), organometallic structures are observed, forming short chains on the surface (**T1**). Upon further annealing, covalent coupling of three activated monomers takes place with two-fold [4+2] cycloadditions for each trimer, which we ascribe to a DDA reaction towards dibenzo[*a,h*]naphtho[2,3-*c*]pentaphene **T2**. Annealing the sample at 300 °C furnishes dibenzo[*abi,lm*]dinaphtho[1,2,3-*fg*:1',2',3'-*uv*]heptacene **T3** via the cyclodehydrogenation of out-of-plane phenyls and the reduction of ethynyl groups at the core.⁴² We speculate that the availability of atomic hydrogen on the Au surface might have led to reduction of the pendent ethynyl groups into vinyl

moieties (see Figure S3 for details). Finally, the steric hindrance between neighboring hydrogens at the cove-edges can result in the occasional formation of five-member rings via intramolecular cyclodehydrogenation,⁴³ leading to e.g. acenaphtho[4,3,2,1-*ab*icd]dibenzo[*fg,uv*]naphtho[3,2,1-*lm*]heptacene **T4** (experimentally imaged).

Products larger than trimers appear as non-regular by STM imaging. We ascribe them to lateral fusion via non-selective CH activation. Here, the DDA reaction between activated precursors **1** can afford products up to trimers leading to an heptacene backbone. This behavior is tentatively attributed to the necessity of simultaneous coupling of the radical positions and cycloadditions involving the ethynyl groups, which makes coupling of more than three monomers impossible, thus yielding only dimers and trimers.

In conclusion, we have reported DDA reactions between bis(phenylethynyl)benzene precursors on an Au(111) surface. Detailed structural characterization of the products at different temperatures reveals the presence of gold-mediated organometallic assemblies as reaction intermediates. The adsorbates subsequently undergo DDA coupling at 200 °C, and are finally converted into planar structures at 300 °C. Heptacene and tetracene core structures are observed on the surface, which is most likely because a simultaneous activation to the radical and the triple bond is required for this on-surface reaction. Our findings demonstrate that the DDA reaction occurs also in two-dimensional space, thus providing an additional tool to the field of on-surface synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental methods; additional reaction schemes and experimental data (PDF).

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Notes

The authors declare no competing financial interests.

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