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## COMMUNICATION

## Cyclotrimerization of Arylalkynes on Au(111)

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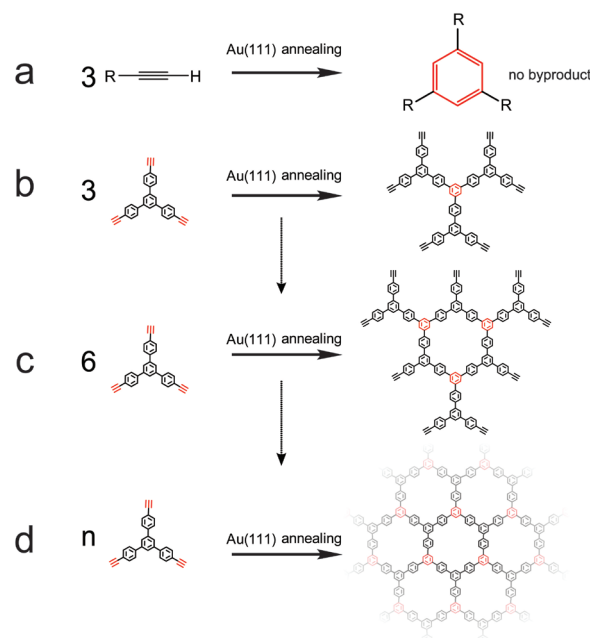
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**Surface-assisted cyclotrimerization of arylalkynes was studied on Au(111) by means of scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. Upon thermal activation, cyclotrimerization of 1,3,5-tris-(4-ethynylphenyl)benzene proceeds readily and with high selectivity, and results in two-dimensional covalently bonded polyphenylene nanostructures exhibiting a honeycomb topology.**

The design and synthesis of two-dimensional (2D) materials has been attracting enormous attention since 2004 when scientists first isolated monolayer graphene sheets<sup>1</sup>. 2D materials are expected to exhibit novel useful properties for applications such as optoelectronics, gas storage or separation, catalysis, sensors, supporting membranes, and anticorrosion<sup>2-4</sup>. Recently many efforts have been made to fabricate 2D inorganic materials, such as graphene, MoS<sub>2</sub><sup>5</sup>, WS<sub>2</sub><sup>6</sup>, BN<sup>7</sup>, or NbSe<sub>2</sub><sup>8</sup>. Simultaneously, there is also strong interest in the fabrication of 2D advanced organic materials, which are cost-effective, plentiful, diverse and easy to process compared to their inorganic counterparts<sup>9</sup>. During the last few years, a novel approach to covalently bonded low-dimensional molecular nanostructures and 2D polymers has emerged – frequently termed “on-surface synthesis” – which is based on the metal surface-assisted covalent coupling of suitably designed molecular precursors under ultrahigh vacuum conditions<sup>10-12</sup>. For example, 2D covalently bonded polymers were obtained from halogen-substituted organic building blocks<sup>13, 14</sup>. Up to now, however, only a limited number of “on-surface” reactions is available to synthesize 2D materials, most prominently aryl-aryl coupling (Ullmann-type reaction)<sup>15, 16</sup>, but also boronic acid condensation<sup>17</sup>, alkyne homocoupling<sup>18</sup>, and a few others<sup>4, 19</sup>. Undoubtedly, the on-surface synthesis “toolbox” needs to be significantly extended to efficiently afford materials with diverse structures and properties.

Most recently, surface reactions of alkynes are intensively studied by using STM<sup>18, 20, 21</sup>. Since the products are connected by conjugated

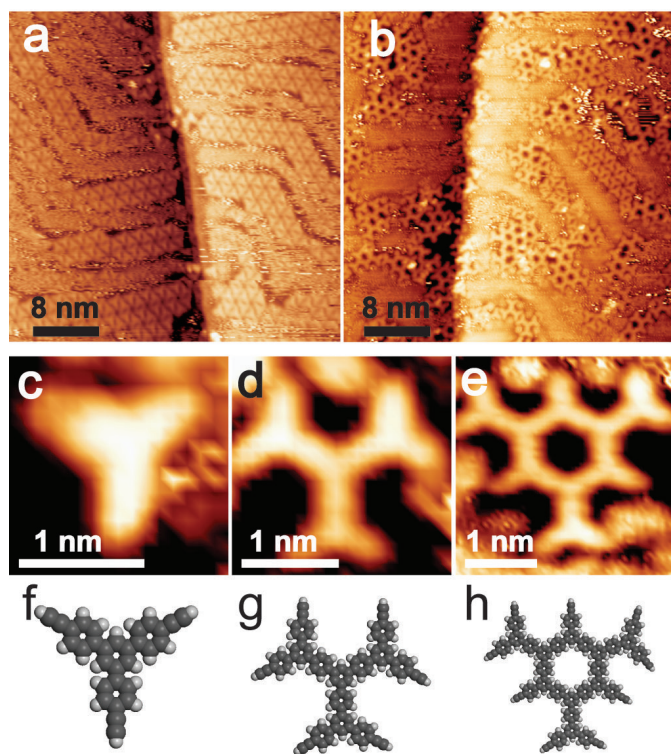
units, these by-product free reactions are highly promising for the synthesis of 1D and 2D functional materials<sup>22, 23</sup>. Results reported so far show that on Ag(111), homocoupling between terminal alkynes is most efficient and selective<sup>18, 20</sup>.



**Scheme 1.** (a) Surface-assisted cyclotrimerization of terminal alkynes on Au(111) triggered by thermal activation. (b-d) Cyclotrimerization of 1,3,5-tris-(4-ethynylphenyl)benzene (TEB) successively produces trimers (b), hexamers with a central empty pore (c), and finally an extended 2D polyphenylene network with honeycomb topology.

On the more reactive Cu(111) surface, different reactions such as homocoupling, trimerization and cross-coupling are found to proceed concurrently<sup>21</sup>, which makes it difficult to control the reaction outcome. On Au(111), Gao et al studied the on-surface coupling of a series of linear arylalkynes with alkyl sidegroups<sup>20</sup>. The

steric shielding of the terminal alkynes was found to largely suppress side reactions and to favor homocoupling. Very recently, polycyclization of a diyne was reported, and discussed in terms of a two-step [2+2+2] cyclization reaction<sup>24</sup>. Herein, we report on the use of 1,3,5-tris-(4-ethynylphenyl)benzene (TEB) as key building block to study on-surface reactions of alkynes on Au(111). We find that cyclotrimerization<sup>25, 26</sup> of TEB is the dominant reaction pathway on Au(111).



**Figure 1.** (a) STM image of TEB molecules self-assembled on Au(111). (b) After annealing at 373 K, surface-assisted cyclotrimerization has only partially proceeded. (c) - (e) STM images of TEB monomer (c), as well as a trimer (d) and hexamer (e) obtained via cyclotrimerization. (f) - (h) depict the corresponding molecular models. Tunneling conditions (current setpoint/bias voltage): (a) 40 pA/1.9 V; (b) 40 pA/0.8 V; (c) 40 pA/0.8 V; (d) 40 pA/0.8 V; (e) 40 pA/0.8 V.

The reaction mechanism for on-surface alkyne cyclotrimerization is illustrated in Scheme 1a: three alkyne groups are thermally activated on the noble metal Au(111) surface and react with each other to form a benzene ring. The molecular structure of the arylalkyne TEB used here is characterized by a three-fold symmetrical aromatic core with three terminal alkyne groups (Scheme 1b) that may be thermally activated to induce cyclotrimerization. After cyclotrimerization three TEB molecules are covalently bonded to each other via a common benzene ring formed from the three alkyne groups. Because there are still unreacted alkyne groups on the trimer, further cyclotrimerization may take place. As illustrated in Scheme 1c and 1d, hexamers with an open pore in the center and a 2D polymer with honeycomb structure may be formed upon further reaction. This scheme – cyclotrimerization of alkynes into arenes – thus bears significant potential for the synthesis of functional 2D polymers with extended conjugation.

STM experiments were performed in a UHV system equipped with an Omicron variable-temperature STM operated at 50 K. Prior to each experiment, the Au(111) surface was cleaned by Ar<sup>+</sup> sputtering and annealing at 743 K for 15 min. After sample cleaning, TEB was deposited from resistively heated quartz crucibles held at 393 K, resulting in deposition rates of about 0.2 monolayer (ML) per minute. Detailed information on the synthesis of TEB can be found elsewhere<sup>27</sup>.

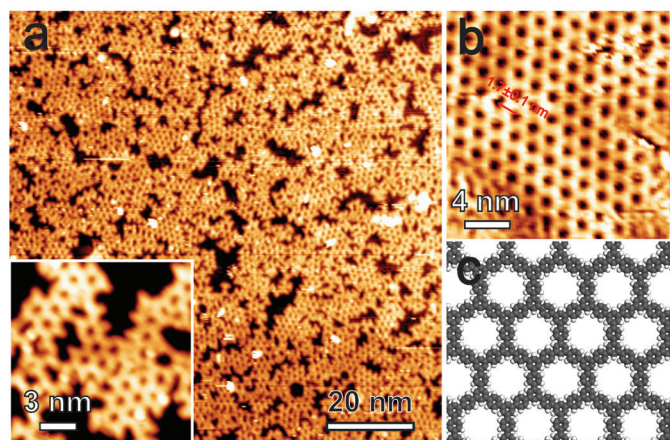
Figure 1a shows a STM topograph of TEB adsorbed on a Au(111) surface that was held at room temperature (RT) during deposition. The molecules exhibit a triangular shape, with three “arms” which can be associated to the ethynylphenyl groups of TEB (Figure 1c,f). Two kinds of domains can be discerned in Fig. 1a. The first one is an ordered self-assembled structure that grows along the herringbone reconstruction lines on fcc substrate lattice regions. It consists of close packed molecules arranged in a ‘windmill’ pattern, with a pore-to-pore distance between neighboring windmills of 1.9 nm. High resolution STM images (Fig. S1 in ESI) show that the molecules are intact and that no reaction happens when the substrate is at RT. The other type of domain is given by disordered areas on hcp substrate lattice regions. The disordered structure is caused by the mobility of the TEB at hcp domains which results in a fuzzy STM appearance. After annealing TEB on Au(111) to 373 K, patches of a 2D network start to appear (Figure 1b). As we will show below, these result from cyclotrimerization of TEB molecules. At this temperature, they coexist with areas of unreacted molecules forming the windmill structure and the same disordered regions seen after RT deposition. Closer inspections of the porous network regions reveals that they occasionally also contain discrete trimers and hexamers such as the ones illustrated in Scheme 1b and 1c. Two examples are given in Figures 1d and 1e, with the corresponding structural models shown in Figures 1g and 1h, respectively. The sizes of these trimers and hexamers as well as their flat and continuous appearance clearly support their identification as the products of the cyclotrimerization of three and six TEB molecules, respectively (see also direct comparison between structural models and STM images in Fig. S2 in ESI).

Upon annealing the TEB/Au(111) sample to higher temperatures, the reaction proceeds further. Figure 2a is an STM image of a sample that was annealed to 433 K. Compared to the sample obtained at 373 K (Figure 1b), after annealing at 433 K the windmill structure has disappeared, and all TEB monomers have reacted. Figure 2a shows that a fully interconnected porous network consisting of small domains of a regular honeycomb structure has been formed. Figure 2b is an STM image of a large domain consisting of nicely formed 2D polyphenylene polymer (we noted that low molecular coverage and slow heating to the reaction temperature generally resulted in larger domains). The pore-to-pore distance is  $1.7 \pm 0.1$  nm, which is well consistent with the polyphenylene structure depicted in Figure 2c. This is significantly larger than the 0.7 nm of the previously reported porous graphene achieved via Ullmann coupling<sup>13</sup>. The latter exhibited pores the size of a single phenyl ring, whereas the polyphenylene structure illustrated in Fig. 2c is conceptually obtained from graphene by the removal of hexa-*peri*-hexabenzocoronene units. From the thermal stability of 805 K reported for the previous porous graphene structure<sup>13</sup>, we anticipate



a high stability for the present system as well. After annealing to 523 K, we find the network unaltered, but we did not explore higher temperatures.

In contrast to the cases of thermally activated arylalkyne reactions on Ag(111) and Cu(111)<sup>18, 20, 21</sup>, cyclotrimerization is the dominant reaction pathway for TEB on Au(111). A detailed analysis of STM images reveals that more than 75% of monomers have undergone cyclotrimerization (Fig. S3 in ESI). Whereas diacetylene formation (homocoupling between terminal alkynes) is only sporadically found at domain boundaries (<5%, Fig. S4 in ESI).



**Figure 2.** (a) Large scale STM image of the 2D polymer network obtained by cyclotrimerization of TEB on Au(111) at 160°C. The inset shows a zoom-in. (b) STM image of a regular domain of the 2D honeycomb polymer, with corresponding structural model depicted in (c). Tunneling conditions (current setpoint/bias voltage): (b) 60 pA/0.7 V; (c) 60 pA/-3.6 V.

As to the details of the surface-assisted cyclotrimerization pathway, it is interesting to consider possible parallels to classical coupling schemes. In solution phase organic synthesis, late transition metals such as Co, Ni, Rh, Ru, Pd, Ir, are commonly utilized in the cyclotrimerization of alkynes<sup>28,29</sup>, which generally proceeds firstly via formation of a metallacyclopentadiene intermediate by two alkynes and one metal atom, followed by insertion of the third alkyne. In UHV, cyclotrimerization of acetylene was studied by spectroscopic methods on various surfaces such as Pd<sup>30</sup> or Cu<sup>31</sup>. A specific focus has been set on cyclotrimerization of acetylene on Pd<sup>32-34</sup>, where the formation of a C<sub>4</sub>H<sub>4</sub> metalocycle intermediate that then reacts with a third acetylene molecule has been identified as the key step. A recent study of acetylene cyclotrimerization on Cu(110) also showed that a C<sub>4</sub>H<sub>4</sub> intermediate was formed<sup>35</sup>. Earlier research on the cyclotrimerization of acetylene on Au(111) in UHV did not reveal any cyclotrimerization<sup>36</sup>, plausibly because of acetylene desorption already below the reaction temperature. For other alkynes, however, significant reactivity on gold surfaces has been reported<sup>37-39</sup>. Considering the central importance of the C<sub>4</sub>H<sub>4</sub> metalocycle intermediates in the reported on-surface cyclotrimerization reactions<sup>32-34</sup>, we suggest a similar scenario for the present case of arylalkyne cyclotrimerization on Au(111). The first step might involve two alkynes reacting with each other to form a metallacyclopentadiene intermediate<sup>26</sup>, which can then further react with a third alkyne. Whether Au adatoms are involved in lowering the corresponding energy barriers, as suggested by recent work on the

cyclotrimerization of a diyne on Au(111)<sup>24</sup>, remains to be explored. Interestingly, a recent computational study of the Ag-surface assisted homocoupling of terminal alkynes has shown that, at least in this case, the reaction path is fundamentally different from the classical coupling schemes in wet chemistry<sup>40</sup>. On Ag(111), homocoupling is initiated by direct C-C bond formation without prior dehydrogenation of the reactants, with the substrate stabilizing the resulting butadiene intermediate. It is clear that similar computational studies are needed to shed further light onto the reaction mechanism of the cyclotrimerization reported here.

In summary, we have demonstrated the on-surface synthesis of a 2D polyphenylene with TEB on Au(111) via cyclotrimerization. The reaction onset is around 373 K, and at 433 K cyclotrimerization is complete. The resulting polymer network is fully interconnected, exhibits extended conjugation, and is thermally stable up to at least 523 K. Since the cyclotrimerization of arylalkynes on Au(111) proceeds readily at modest temperatures, the presented approach bears promise for the fabrication of 2D networks and functional arenes with useful electronic properties. The reaction taking place on a Au(111) noble metal surface under soft reaction conditions also brings a new view to transition-metal-catalyzed cyclotrimerization reactions.

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## Notes and references

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