

## Nanotrough Arrays

## Surface-Assisted Organic Synthesis of Hyperbenzene Nanotroughs\*\*

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The surface-assisted synthesis of organic molecules and nanostructures is a promising bottom-up approach towards functional surfaces for applications in catalysis, sensor systems, and organic electronics. The major challenge of this approach is that most established C-C coupling reactions require solvents and thus cannot be performed on solid surfaces under ultrahigh vacuum (UHV) conditions. One of the few exceptions<sup>[1]</sup> is the Ullmann reaction,<sup>[2]</sup> which achieves C-C coupling between haloarene molecules by means of metallic Cu. First reported in 1901, it is one of the oldest heterogeneous reactions of organic chemistry and has recently been employed, in a modified form, in attempts to prepare one- and two-dimensional (1D/2D) polymers on metal single-crystal surfaces.<sup>[3-10]</sup> 2D covalent networks in particular have attracted great interest for the nanostructuring of functional surfaces.<sup>[11-14]</sup> The synthesis of 2D networks was especially successful for systems in which the monomers are linked by relatively weak bonds, such as coordinative or hydrogen bonds.<sup>[15,16]</sup> Formation of these bonds is reversible, which allows the system to reach a local energy minimum by "healing" of initial defects in the long-range order of the network. In contrast, formation of C-C bonds is usually not reversible and thus defects will persist. For this reason, covalent 2D networks grown from molecular precursors often contain a wide range of local binding motifs, that is, many defects.<sup>[11,13,17]</sup> A notable exception is graphene, which can be

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[**]	J.F.Z. thanks the National Natural Science Foundation of China (Grant No.21173200), the Specialized Research Fund for the Doctoral Program of Higher Education of Ministry of Education (Grant No. 20113402110029), and the National Basic Research Program of China (2010CB923302). W.H. thanks the Deutsche Forschungsgemeinschaft and the Cluster of Excellence "Engineer- ing of Advanced Materials" granted to the University of Erlangen- Nürnberg, I.M.G. thanks the Chinese Academy of Sciences for

No. 2011T2J33). Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201300610.

a Visiting Professorship for senior international scientists (Grant

grown on surfaces defect-free over large areas, because it represents the global energy minimum and thus can be synthesized under conditions at which the C–C bond formation becomes reversible, in particular at high temperatures.<sup>[4,18-21]</sup>

In the light of this fundamental problem, we pursue herein a hierarchic strategy and first synthesize, directly on a copper-(111) surface, C–C-bonded molecular subunits, which then assemble to form van der Waals bonded arrays. This approach takes into account the fact that small units with fewer degrees of freedom can structurally more easily be controlled than large units, which becomes an important point when bond formation is irreversible. The synthesis of small molecules on surfaces using the Ullmann reaction is possible, as has been shown for biphenyl.<sup>[22-24]</sup> The reaction steps can even be controlled by manipulation with a scanning tunneling microsope (STM).<sup>[25]</sup> However, attempts to synthesize large cyclic molecules on surfaces have not yet been successful;<sup>[26]</sup> only sexiphenylene was observed as a minor byproduct in the synthesis of oligophenylene chains.<sup>[6]</sup>

Herein we used 4,4"-dibromo-1,1':3',1"-terphenyl (1; 4,4"dibromo-m-terphenyl, DMTP; Scheme 1) as a precursor monomer and Cu(111) as the substrate for the surfaceassisted synthesis. A (111) surface was chosen because its hexagonal symmetry was shown to stabilize angles of 120° in the adsorbate lattice owing to template effects.<sup>[27]</sup> Physical vapor deposition of DMTP onto the clean Cu(111) surface held at 300 K leads to cleavage of the Br-C bonds, as confirmed by X-ray photoelectron spectroscopy (XPS; see the Supporting Information, Figure S1) and in agreement with previous work.<sup>[28]</sup> The STM images displayed in Figure 1 show that the *m*-terphenylene fragments form elongated islands consisting of zigzag chains, which have preferential orientations relative to the high-symmetry directions of the Cu(111) substrate (see the Figure caption for details). The lattice constant *along* the chains is 26.5 Å (Figure 1b). This is larger than expected for direct C-C linkage (which would lead to a lattice constant of 21.8 Å) and thus suggests that the *m*-terphenylene fragment are linked by Cu atoms, forming the 1D coordination polymer 2 (see Scheme 1). This conclusion is supported by the density functional theory (DFT) calculations described below, which predict a lattice constant along the chains of 26.5 Å for the C-Cu-C bonded coordination polymer, and agrees with a previous publication about 4,4"dibromo-p-terphenyl on Cu(111),<sup>[28]</sup> in which linear coordination polymer chains with C-Cu-C bonds were reported. The apparent height in STM varies along the chains, and the terphenyl units (located at the bends; large maxima in Figure 1 g) can be distinguished from the C-Cu-C bridges (at the straight parts of the chain; small maxima in Figure 1g).



**Scheme 1.** Surface-assisted Ullmann coupling reaction of 4,4"dibromo-*m*-terphenyl 1 forming a) the coordination polymer **2** at 300 K and b) hyperbenzene molecules **3** at 550 K on Cu(111).

The extreme aspect ratio of the islands (up to 1:25) shows that chain growth is much more likely than the start of a new chain. The assembly of the individual chains to islands is apparently driven by van der Waals forces (as opposed to covalent or coordinative bonds), as indicated by the large distance of 9.7 Å between the chains (measured perpendicular to the straight parts of the zigzag chains). Owing to the 120° bend in molecular subunits, the chains can back-fold at the end of an island, such that islands often consist of only a single chain or very few chains, or that a chain continues from one island to another island with a different orientation (Figure 1 a,c). Occasionally, isolated hexagons with a diameter of 25.2 Å were observed, which, by size considerations, consist of six *m*-terphenylene units linked by Cu atoms (Figure 1c, inset). Deposition of DMTP onto Cu(111) held at 440 K (Figure 1 d) also yields islands of the 1D coordination polymer that are larger than those obtained at 300 K and can exceed 200 nm in length and width (Supporting Information, Figure S2), with defect-free areas larger than  $30 \text{ nm} \times$ 60 nm. However, also at this temperature no C-C bond formation is observed.

Completely different structures are formed when the Cu(111) sample is held at 550 K during deposition of DMTP: As shown in Figure 2, ordered arrays of hexagonal rings with a diameter of 21.3 Å are obtained besides chain-like and other structures. Size comparison shows that each hexagonal ring is built up of six *m*-terphenylene fragments (one at each corner) and thus contains 18 phenylene groups. The macrocycle can therefore be referred to as cyclo-octadecaphenylene. Motivated by its hexagonal structure and in analogy to the much smaller coronene, which is also known as "superbenzene", the



Figure 1. Coordination polymers and oligomers with C-Cu-C bonds: a) Constant-current STM image after deposition of DMTP 1 onto Cu(111) at 300 K at low coverage; tunneling parameters U = -3.6 V, I = 0.02 nA. The islands consist of chains of the coordination polymer **2**, which are oriented at angles of  $\pm 5^{\circ}$  relative to a set of substrate high-symmetry directions ([110] and equivalent), as marked with green arrows. b) Higher-resolution image of the shaded area in (a) with overlaid molecular model and unit cell, U = -3.6 V, I = 0.01 nA. c) The coordination polymer **2** at higher precursor coverage, U = -2.75 V, I = 0.08 nA. Inset: Magnified view of a hexagonal cyclic coordination hexamer superimposed with a molecular model. d) After deposition of 1 onto Cu(111) held at 440 K, which leads to larger islands of the coordination polymer **2**; U = -3.6 V, I = 0.02 nA. e) Side view of a structure from periodic DFT calculations, illustrating the non-planar geometry of the chains. f) DFT-calculated STM image for the tunneling parameters in (b). g) Apparent height profile along the blue zigzag line in (b) from left to right.

new molecule will be denoted "hyperbenzene" in the following.

Formation of one hyperbenzene molecule requires formation of six new C–C bonds. In line with this, the variation of the apparent height along the ring is small compared to the case of the coordination oligomers (compare the height profile in Figure 2e with Figure 1g). Furthermore, the corner-



**Figure 2.** Hyperbenzene: a) Overview constant-current STM image obtained at 300 K after deposition of DMTP 1 onto Cu(111) held at 550 K. The hexagonal rings **3** (hyperbenzene) show a preferential orientation relative to the high-symmetry directions of the substrate. b) Magnified view of a small section with oligophenylene chains. c) Magnified view of a hyperbenzene **3** island with several defects and inclusions in the central cavities. Molecular models and a unit cell are overlaid. Tunneling parameters: U = -3.6 V, I = 0.01 nA. d) DFT-calculated STM images for U = -3.6 V and I = 0.01 nA with overlaid model of the relaxed computed structure. e) Apparent height profile along the perimeter of a hyperbenzene molecule, as marked by the blue hexagon in the inset. Note that the height axis is identical to that in Figure 1 g to allow direct comparison.

to-corner distance is only 12.3 Å (12.9 Å according to DFT calculations; see below). This is almost 2 Å less than the bend-to-bend distance in the coordination polymer chains (STM: 15.1 Å, DFT: 15.3 Å). Furthermore, the ring diameter is almost 4 Å smaller than the diameter of the cyclic coordination hexamer (Figure 1 c, inset). These contractions and their agreement with the results of DFT calculations (see below) provide additional evidence that the fragments are now connected by C–C bonds instead of C-Cu-C bonds.

Hyperbenzene forms a hexagonal lattice on Cu(111); the unit cell dimensions are shown in Figure 2c. The small deviations from the ideal unit cell geometry are due to residual thermal drift during the STM imaging. The distance between the edges of two adjacent hyperbenzene molecules is 9.3 Å; this distance is almost identical to the distance between the coordination polymer chains in Figure 1, which shows that the assembly is mainly driven by van der Waals interactions and that there are no C–C bonds between the rings.

No rings smaller than hyperbenzene were observed. Apparently, the combination of a rigid molecular precursor with a substrate of hexagonal symmetry, which favors the 120° angle, leads to a certain selectivity of the reaction with respect to the ring systems formed. The template influence of the surface is also evident from the preferential orientation of the hyperbenzene islands relative to the high-symmetry directions of the substrate (Figure 2 a).

We note that the surface-assisted synthesis reported herein is presently the only feasible method to prepare adsorbed hyperbenzene arrays, because vapor deposition of hyperbenzene (which has not been synthesized in solution yet) on a surface would not be possible owing to the high molecular weight of 1369.7 g mol<sup>-1</sup> based on the nominal formula  $C_{108}H_{72}$ . Apart from deposition from solution (which is likely to result in contaminated layers), electrospray ionbeam deposition, which is a complex and rarely applied technique, would be a possible approach.<sup>[29]</sup>

Apart from the arrays of hyperbenzene molecules, small areas with short zigzag chains are observed after deposition of DMTP at 550 K (Figure 2b). Compared to the zigzag coordination polymer in Figure 1, the unit cell is contracted along the chains (from 26.5 Å to 21.8 Å) and the bend-tobend distance is reduced from 15.1 Å to 12.5 Å, a value very close to the corner-to-corner distance in the hyperbenzene rings (12.3 Å), while the distance between the chains remains unchanged. Furthermore, the brightness along the chains is now almost uniform. These changes indicate that the terphenylene units are connected by C–C bonds; that is, oligophenylene chains are formed.

While most of the nanotroughs shown in Figure 2 appear to be empty, occasionally circular-shaped objects can be observed inside the cavities. Most likely this is a molecule or molecular fragment that rotates on a time scale faster than imaging, illustrating that the nanotroughs can indeed enclose molecular objects.

To obtain more detailed insight into the structural properties of the described nanoobjects, we have performed periodic dispersion-corrected density-functional calculations on the coordination polymer 2 and the hyperbenzene molecule 3, both adsorbed on a Cu(111) slab (see the Experimental Section for details). The adsorption structure and simulated STM images are shown in Figure 1e,f and 2d. The polymer 2 adopts a buckled, non-planar geometry on the Cu(111) surface (Figure 1e), with the Cu atoms in the polymer in close proximity to the Cu(111) surface, and the central phenylene ring of the terphenylene units at larger distance from the surface than the other two rings; in total, the height varies by 0.9 Å between the C atom with the largest value of the z coordinate and the coordinated Cu atom, which has the lowest value of the z coordinate. This peculiar structure of 2 on Cu(111) has an impact on its STM image. In both the experimental and simulated STM (Figure 1b,f), the bends of the coordination polymer, which can be identified as the central rings of the terphenylene units, appear as bright protrusions, reflecting their elevation from the surface. The linking Cu atoms in the polymer, on the other hand, are imaged in the STM as rather weak spots, reflecting their large distance from the tip. The experimental variation of the apparent height is smaller (ca. 0.2 Å; see Figure 1g) than the theoretical value, which is attributed to superimposed electronic effects, especially to the more efficient tunneling through the coordinated metal centers, which makes them appear more elevated than they are. Such effects have previously been observed for organometallic compounds.<sup>[30, 31]</sup> The simulated STM image of the macrocycle 3 is displayed in Figure 2d. It shows almost uniform contrast over the complete macrocycle and the absence of the Cu links present in polymer 2. A graphical representation of the adsorption structure can be found in the Supporting Information, Figure S4.

In summary, arrays of hexagonal hyperbenzene nanotroughs were synthesized directly on a copper surface from 4,4"-dibromo-m-terphenyl by multiple C–C coupling with the Ullmann reaction. As possible precursors to the formation of hyperbenzene, zigzag-shaped and cyclic coordination oligoand polymers with C-Cu-C bonds have been observed. Each hyperbenzene molecule contains six precursor molecules and thus requires the formation of six new C–C bonds. The hyperbenzene molecules aggregate to ordered arrays with a hexagonal unit cell, a process that is driven by van der Waals interactions. Owing to the large diameter of 21.3 Å, the nanotroughs could enclose a wide range of quantum dots, such as metal and semiconductor particles or large organic molecules.

## **Experimental Section**

DMTP (1) was synthesized from 4-bromophenylacetylene in a short reaction sequence utilizing a Grubbs enyne metathesis reaction and a regioselective cobalt-catalyzed Diels–Alder reaction followed by mild oxidation (see the Supporting Information) and was vapor-deposited in the vacuum from an effusion cell evaporator held at 360 K onto a Cu(111) single crystal (MaTecK GmbH, Germany) with a typical flux of 0.11 MLmin<sup>-1 [32]</sup> STM images were recorded with a SPECS STM 150 Aarhus with SPECS 260 electronics at room temperature. All given voltages are referred to the sample and the images were taken in constant-current mode.

Periodic density-functional calculations were performed with the Vienna ab initio simulation package (VASP)<sup>[33]</sup> using the PBE functional<sup>[34]</sup> in combination with a van der Waals dispersion correction<sup>[35]</sup> and the projector-augmented wave method.<sup>[36]</sup> The adsorbate structures have been relaxed along with the top two copper layers of five-layer Cu(111) slabs. The constant-current STM simulations are based on the Tersoff–Hamann model.<sup>[37]</sup> More details of the calculations can be found in the Supporting Information.

Received: January 23, 2013 Published online: March 19, 2013

Keywords: hyperbenzene · macrocycles ·

scanning probe microscopy · self-assembled monolayers · Ullmann reaction

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